

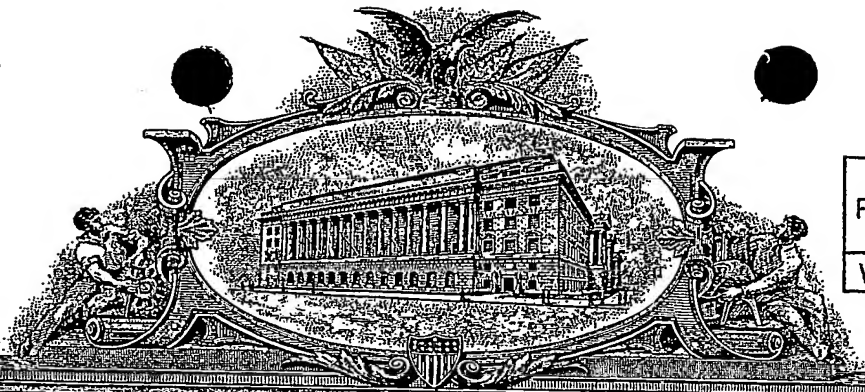
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FILING DATE.**

APPLICATION NUMBER: 60/302,052

FILING DATE: June 29, 2001

RELATED PCT APPLICATION NUMBER: PCT/US02/20973



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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53 (c).

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JC979 U.S. PTO
60/302052
06/29/01

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Matthew A.	Odom	Longmont, CO		
<input checked="" type="checkbox"/> Additional inventors are being named on the 1 separately numbered sheets attached hereto				
TITLE OF THE INVENTION (280 characters max)				
EXTRACTION AND RECOVERY OF IONS FROM A SOLUTION				
CORRESPONDENCE ADDRESS				
Direct all correspondence to:				
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ENCLOSED APPLICATION PARTS (check all that apply)				
<input checked="" type="checkbox"/> Specification Number of Pages	28	<input type="checkbox"/> CD(s), Number		
<input checked="" type="checkbox"/> Drawing(s) Number of Sheets	4	<input checked="" type="checkbox"/> Other (specify)	30 Attachment	
<input checked="" type="checkbox"/> Application Data Sheet. See 37 CFR 1.76				
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT				
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				
<input type="checkbox"/> A check or money order is enclosed to cover the filing fees				
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:				
20-1430		FILING FEE AMOUNT (\$)		
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.				
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<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are:				

Respectfully submitted,

SIGNATURE

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TELEPHONE 303-571-4000

Date

06/29/01

REGISTRATION NO. 40,945
(If appropriate)

Docket Number:

019397-000400US

Client No. 00-001

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

J1129 U.S. PTO

60302052-062901

PROVISIONAL APPLICATION COVER SHEET
Additional Page

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Docket Number	19397-000400US Client No. 00-001	Type a plus sign (+) Inside this box →	+
INVENTOR(S)/APPLICANT(S)			
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Number 2 of 2

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DE 7044073 v1

60302052.062901

**FEE TRANSMITTAL
for FY 2001**

Patent fees are subject to annual revision.

Complete if Known

Application Number

Filing Date

First Named Inventor

Strauss, Steven H.

Examiner Name

Group Art Unit

Attorney Docket No.

019397-000400US

TOTAL AMOUNT OF PAYMENT

(\$)
75

METHOD OF PAYMENT

1. ☒

The Commissioner is hereby authorized to charge indicated fees and credit any over payments to:

Deposit
Account
Number

20-1430

Deposit
Account
Name

Townsend and Townsend and Crew LLP

- ☒ Charge Any Additional Fee Required
Under 37 CFR 1.16 and 1.17
☒ Applicant claims small entity status.
See 37 CFR 1.27

2. ☐ Payment Enclosed:

- ☐ Check ☐ Credit card ☐ Money
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FEE CALCULATION

1. BASIC FILING FEE

Large Fee Code	Entity Fee (\$)	Small Fee Code	Entity Fee (\$)	Fee Description	Fee Paid
101	710	201	355	Utility filing fee	
106	320	206	160	Design filing fee	
107	490	207	245	Plant filing fee	
108	710	208	355	Reissue filing fee	
114	150	214	75	Provisional filing fee	75

SUBTOTAL (1)

(\$)
75

2. EXTRA CLAIM FEES

Total Claims		-20**	=	Extra Claims	X	Fee from below	=	Fee Paid
Independent Claims		-3**	=		X		=	
Multiple Dependent					X		=	

Large Fee Code	Entity Fee (\$)	Small Fee Code	Entity Fee (\$)	Fee Description
103	18	203	9	Claims in excess of 20
102	80	202	40	Independent claims in excess of 3
104	270	204	135	Multiple dependent claim, if not paid
109	80	209	40	** Reissue independent claims over original patent
110	18	210	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2)

(\$)
0

**or number previously paid, if greater; For Reissues, see above

FEE CALCULATION (continued)

Large Fee Code	Entity Fee (\$)	Small Fee Code	Entity Fee (\$)	Fee Description	Fee Paid
105	130	205	65	Surcharge - late filing fee or oath	
127	50	227	25	Surcharge - late provisional filing fee or cover sheet	
139	130	139	130	Non-English specification	
147	2,520	147	2,520	For filing a request for reexamination	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	
115	110	215	55	Extension for reply within first month	
116	390	216	195	Extension for reply within second month	
117	890	217	445	Extension for reply within third month	
118	1,390	218	695	Extension for reply within fourth month	
128	1,890	228	945	Extension for reply within fifth month	
119	310	219	155	Notice of Appeal	
120	310	220	155	Filing a brief in support of an appeal	
121	270	221	135	Request for oral hearing	
138	1,510	138	1,510	Petition to institute a public use proceeding	
140	110	240	55	Petition to revive - unavoidable	
141	1,240	241	620	Petition to revive - unintentional	
142	1,240	242	620	Utility issue fee (or reissue)	
143	440	243	220	Design issue fee	
144	600	244	300	Plant issue fee	
122	130	122	130	Petitions to the Commissioner	
123	50	123	50	Petitions related to provisional applications	
126	180	126	180	Submission of Information Disclosure Stmt	
581	40	581	40	Recording each patent assignment per property (times number of properties)	
146	710	246	355	Filing a submission after final rejection (37 CFR § 1.129(a))	
149	710	249	355	For each additional invention to be examined (37 CFR § 1.129(b))	
179	710	279	355	Request for Continued Examination (RCE)	
169	900	169	900	Request for expedited examination of a design application	

Other fee (specify)

The Commissioner is authorized to charge any additional fees to the above noted Deposit Account.

*Reduced by Basic Filing Fee Paid

SUBTOTAL (3)

(\$)
0

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303-571-4000

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Date

June 29, 2001

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106290-25020009

Application Information

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Filing Date:: / /
Application Type:: Provisional
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A SOLUTION
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Request for Non-Publication:: No
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Petition included?:: No
Secrecy Order in Patent Appl.?:: No

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PROVISIONAL PATENT APPLICATION

EXTRACTION AND RECOVERY OF IONS FROM A SOLUTION

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106290-25020509

EXTRACTION AND RECOVERY OF IONS FROM A SOLUTION

FIELD OF THE INVENTION

[01] The present invention is directed to a solid ion-extractant comprising a solid support and an ion-coordinating agent and a method for using the same.

BACKGROUND OF THE INVENTION

[02] One of the most commonly used method for removing a particular type of ions from a solution involves an ion-exchange process in which the ion to be removed from the solution is exchanged with a different ion using a solid ion-exchange resin. Generally, this process involves reversible exchange of ions between a liquid phase (*i.e.*, the solution) and a solid phase (*i.e.*, ion-exchange resin). The "extracted" ions are then typically recovered as a solution using another ion exchange process or as a part of the solid phase. The latter recovery process is undesirable as this requires a fresh supply of the solid ion-exchange resin for each ion extraction and recovery process. If the ions (specifically, the corresponding salts) are relatively insoluble, then the former recovery process requires a large volume of solvent to recover the extracted ions.

[03] Perfluoroalkylsulfonates (PFS's), *e.g.*, $C_nF_{2n+1}SO_3^-$, typically having potassium counter cation, are widely used as foaming agents, *e.g.*, in fighting fires. While PFS's are vital ingredients in fire fighting, they are undesirable pollutants in water supply. These PFS's in waste water poses problem to water treatment facilities as they tend to cause foaming and are difficult to remove. Moreover, PFS's are both chemically and thermally very stable; therefore, they cannot be easily removed from water or destroyed by a simple chemical or thermal process. Currently, there is no effective method of efficiently removing PFS's from waste water. Furthermore, because PFS's are relatively insoluble in water at a relatively low temperature, *i.e.*, at or below ambient temperature, even if they are removed from water by an ion-exchange process, a relatively large amount of water is required to recover the extracted PFS's. Moreover, current ion-exchange resins are not particularly selective for PFS's, thus necessitating the use of a large excess of ion-exchange resins.

[04] Therefore, there is a need for a method for removing and recovering PFS's from an aqueous solution which does not require a large volume of recovery water. There is also a need for an ion-exchange resin which is selective for PFS's.

BRIEF SUMMARY OF THE INVENTION

[05] The present invention is directed to methods and compounds which are useful in extracting ions from a solution. Preferably, the ion has different solubility at different solvent temperatures. For example, the ion can be highly soluble at a low solvent temperature and only sparingly soluble at a high solvent temperature. Or the ion can be only sparingly soluble at a low solvent temperature and highly soluble at a high solvent temperature. Preferably, the solubility ratio between the ion with its corresponding counter ion at a solvent temperature of 50 °C or above and at a solvent temperature of less than 30 °C is at least about 5, more preferably at least about 10, still more preferably at least about 100, and most preferably at least about 1000. The ion can be anion or cation.

BRIEF DESCRIPTION OF THE DRAWINGS

[06] Figure 1 is a schematic drawing of a method for removing and recovering ions of the present invention;

[07] Figure 2 shows exemplary coupling catalysts which are useful in preparing the extractant compounds of the present invention from the corresponding olefins and silane compounds;

[08] Figure 3 shows concentration of PFS anions before and after extraction with $\text{HEP}^+\text{NO}_3^-/\text{XAD-7}$; and

[09] Figure 4 shows a relative NIEMS intensities of PFS anions recovered from the cold trap during the PFS anion extraction and recovery process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[10] This detailed description of the invention is presented for purposes of convenience and illustration for the case of removing perfluoroalkylsulfonates from an aqueous solution. It is to be understood, however, that the invention as a whole is not intended to be so limited, and that one skilled in the art will recognize that the concept of the invention will be applicable to removing other ions, which are relatively insoluble at a given solvent temperature range, from both aqueous and non-aqueous solutions, *e.g.*, organic solutions, in accordance with the techniques discussed herein. Other ions suitable for removal and recovery using the present invention will be readily apparent to those skilled in the art.

[11] A method for removing and recovering PFS's from aqueous layer will now be described with regard to the accompanying drawings which assist in illustrating various features of the invention. In this regard, the present invention generally relates to removing and recovering ions of salts which are relatively insoluble from a solution. In particular, the present invention relates to removing and recovering PFS's from an aqueous solution.

[12] It should be appreciated that ions, such as PFS anions, of the present invention themselves do not necessarily comprise chemical compounds which can be isolated. Indeed, in an isolable compound, ions such as PFS anions must be paired with cations to maintain electroneutrality. Thus, it is to be understood that isolation or recovery of an ion refers to isolation or recovery of its corresponding salt.

[13] One particular embodiment of a method for removing PFS's from an aqueous solution is generally illustrated in Figure 1, which is provided for the sole purpose of illustrating the practice of the present invention. Figure 1 does not constitute limitations on the scope of the present invention.

[14] Alkali metal, e.g., potassium, sodium or lithium, salts of PFS anions which are used as foaming agents in fire fighting are relatively insoluble, *i.e.*, solubility of less than about 1 g/L, in water at ambient temperature (*i.e.*, room temperature). These PFS salts in wastewater cause foaming and are difficult to remove by current conventional wastewater treatment processes. Moreover, because PFS ions are both chemically and thermally stable, they are difficult to remove from wastewater. One possible method of removing PFS ions from wastewater (or from an aqueous solution in general) is to use an ion-exchange process. Unfortunately, due to low solubility in water, a large volume of water is required to recover PFS's from the ion-exchange resin, which defeats the purpose of trying to remove PFS's from water in the first place. Moreover, use of a fresh source of ion-exchange resin for each PFS extraction process is economically not feasible.

[15] The present inventors have discovered a new extraction and isolation method which takes advantage of the low solubility of PFS anions. Moreover, the present inventors have discovered a new solid ion-extractant which is specific for coordinating PFS anions relative to other smaller anions such as halides, including chloride, bromide and iodide; nitrate; phosphate; and other similar anions.

[16] The solid ion-extractant of the present invention can be activated and deactivated to allow coordination and release, respectively, of PFS anions, thereby making the extraction and recovery of PFS anions extremely simple.

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[17] As discussed in detail below, when the solid ion-extractant of the present invention is deactivated, the PFS anions which have been concentrated on the solid-ion extractant are released and precipitates on or near the solid ion-extractant. One method of removing these PFS's is to use a large volume of water to dissolve all the PFS's and to recover PFS's as another aqueous solution. This requires removal of a large volume of water to isolate the PFS's, which requires a large amount of time and energy. By using the extraction and recovery process of the present invention, the volume of water required to remove extracted PFS's are significantly reduced. Furthermore, methods of the present invention allow a simple and facile recovery of the extracted PFS's.

[18] As shown in Figure 1, a column 10 of solid ion-extractant, discussed in detail below, is activated by adding a solution containing an ion-extractant activating compound. An aqueous solution containing PFS anions is then passed through the activated solid ion-extractant. This removes (*i.e.*, extracts) PFS anions from the aqueous solution and concentrates them on or near the solid ion-extractant. The amount of solid ion-extractant used depends on the amount of PFS's present in the aqueous solution as well as the amount of ion-extractant compound present in the solid ion-extractant. Typically, the total amount of ion-extractant compound in the column 10 is from about 1.4 to about 1.8 times the amount of total PFS anions present in the aqueous solution. The rate of aqueous solution flow through the column 10 affects the efficiency of PFS anion removal. Generally, the faster the flow rate, less efficient the removal.

[19] The column 10 can be interconnected to a detector 14 to determine whether the effluent aqueous solution from column 10 contains PFS anions. Exemplary detectors which are useful in detecting ions present in an aqueous solution include an Fourier Transform Infrared (FTIR) detector, in particular FTIR detector described in a commonly assigned U.S. Provisional Patent Application No. 60/227,758, entitled "Detection of Ions in a Fluid Medium" filed on August 24, 2000, which is further identified by Attorney Docket No. 019397-000500US, which is incorporated herein by reference in its entirety.

[20] After extracting PFS's, the column 10 is flushed with an ion-extractant deactivating solution. This results in precipitation and/or release of concentrated PFS salts from the solid ion-extractant. The column is then flushed with water that is at least about 85 °C, which dissolves PFS salts. It has been found by the present inventors that the solubility of PFS salts increases as the temperature of water increases. Thus, methods of the present

invention utilizes this difference in solubility of PFS salts in different water temperature to isolate (i.e., recover) PFS salts from an aqueous solution.

[21] The resulting hot water which contains dissolved PFS salts is then cooled by a chiller 18 to precipitate dissolved PFS salts. The solid PFS salts is then separated, e.g., by filtration, centrifugation or by other solid-liquid separation techniques known to one of ordinary skill in the art.

[22] To minimize the volume of water used in the process, the separated water can be reheated by the heater 22 and reused to further remove PFS salts from the column 10. In this manner, a significantly small volume of water can be used to recover PFS salts by using a recirculating water pump 26, which may be located anywhere along the recirculating path.

[23] After PFS salts have been removed from the column 10, the solid ion-extractant can be reactivated by introducing a solution of activating, e.g., oxidizing, agent through the column 10. In this manner, the solid ion-extractant can be recycled and reused.

[24] Methods of the present invention can also include providing a valve systems (30 and 34) which allows introduction and removal of activating or deactivating agents through a different source than the PFS salt recovery water source. This reduces or prevents PFS salts being contaminated with the activating and/or deactivating agents. Contamination can be further reduced by flushing the column 10 with cold water, i.e., less than about 5 °C, after activating or deactivating the solid ion-extractant in the column 10, thereby removing residual activating or deactivating agents which may be present in the column 10.

[25] The solid ion-extractant of the present invention includes a solid support and an ion-coordinating moiety (i.e., extractant compound), which are covalently bonded.

[26] Preferably, the solid support is a glass or a polymeric resin. Exemplary polymeric resins which are useful in the present invention include, but not limited to, acrylic esters (e.g., Supelco® XAD-7 and DAX-8), polyvinyls, polystyrenes, polypyrroles, polyolefins, and polyaromatics (e.g., Supelco® XAD-1180). Preferably the polymeric resin is selected from the group consisting of polydivinylbenzene, polyvinylchloride, polyvinyl alcohol, polystyrene, polypyrrole, polymethacrylate, and functionalized polyolefin, more preferably from the group consisting of polystyrene, polymethacrylate and polyacrylic ester, and most preferably from the group consisting of polyacrylic ester.

[27] Preferably, the ion-extractant has a high selectivity for PFS anions.

The ion-extractant compound of the present invention can include a lipophilic portion which provides increased interaction with and/or selectivity for PFS's in the aqueous solution.

Preferably, the ion-extractant compounds are redox-recyclable compounds. As used herein, a

5 "redox-recyclable compound" refers to an ion-extractant compound which can be activated and deactivated by oxidation and reduction, respectively. For example, typically the ion-extractant compound is a neutral compound which is oxidized (i.e., activated) to a cation containing a corresponding anion. Useful corresponding anions include, but are not limited to, nitrate (NO_3^-), halide (e.g., F^- , Cl^- , Br^- and I^-), HSO_4^- , ClO_4^- , ReO_4^- , PF_6^- , carboxylates
10 (e.g., acetate) and CF_3SO_3^- . When this oxidized ion-extractant compound is contacted with an aqueous solution containing PFS anions, it undergoes exchange of anions, thereby concentrating PFS anions onto the solid ion-extractant. The concentrated PFS's can be removed from the solid ion-extractant by simply reducing (i.e., deactivating) the extractant compound to regenerate the neutral extractant compound. In this manner, the solid ion-extractant can be activated and deactivated rapidly and reused repeatedly.

[28] The ion-extractant compounds of the present invention can be reduced and oxidized using a chemical reducing agent and a chemical oxidizing agent, respectively, or by electrochemically. Exemplary chemical oxidizing agents include, but are not limited to, $\text{Fe}(\text{NO}_3)_3$, AgNO_3 , FeCl_3 , AgF , NaOCl , $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ and $\text{Ce}(\text{SO}_4)_2$. Preferably, the
20 oxidizing agent is selected from the group consisting of $\text{Fe}(\text{NO}_3)_3$, AgNO_3 , FeCl_3 and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, more preferably from the group consisting of $\text{Fe}(\text{NO}_3)_3$, AgNO_3 and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, and most preferably from the group consisting of $\text{Fe}(\text{NO}_3)_3$ and AgNO_3 . Exemplary chemical reducing agents include, but are not limited to, $\text{Na}_4\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{Na}_2\text{S}_2\text{O}_4$, Cr^{2+} salts, V^{2+} salts and NaBH_4 . Preferably, the reducing agent is selected from the
25 group consisting of $\text{Na}_4\text{Fe}(\text{CN})_6$, $\text{Na}_2\text{S}_2\text{O}_4$, NaBH_4 and Cr^{2+} salt, more preferably from the group consisting of $\text{Na}_4\text{Fe}(\text{CN})_6$, $\text{Na}_2\text{S}_2\text{O}_4$ and NaBH_4 , and most preferably from the group consisting of $\text{Na}_4\text{Fe}(\text{CN})_6$ and $\text{Na}_2\text{S}_2\text{O}_4$.

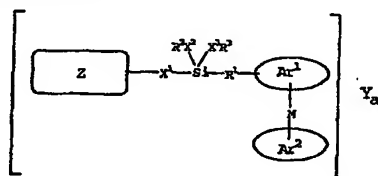
[29] In one particular embodiment of the present invention, the ion-extractant compounds are organometallic compounds (e.g., transition-metal complexes) that
30 are very stable as neutral complexes and as one-electron oxidized cations. Ion-extractant compounds of the present invention are substantially kinetically inert to substitution in both redox states. Preferably ion-extractant compounds of the present invention include polydentate ligands. Moreover, it is also preferred that the ion-extractant compounds do not contain acid- or base-labile functional groups.

[30] Preferably, the ion-extractant compounds of the present invention have redox potentials that allow the use of simple, inexpensive oxidants or reductants and undergo rapid one-electron oxidation or reduction. Moreover, it is preferred that the ion-extractant compounds do not undergo over-oxidation or over-reduction in the presence of an excess of oxidant or reductant, respectively. Preferably, the ion-extractant compounds are relatively nontoxic (e.g., iron complexes are preferred to chromium complexes).

[31] Preferably, the ion-extractant compounds of the present invention are relatively inexpensive (e.g., iron complexes are preferred to ruthenium complexes). Furthermore, the ion-extractant compounds of the present invention have negligible water solubility in both working oxidation states. For example, for removing and recovering a large and weakly-hydrated anions, such as PFS anions, the ion-extractant compounds are selected from salts of a large, lipophilic cation having a small hydrophilic counter anion, because the large size of the ion-extractant compound increases the selectivity of the solid ion-extractant for the large anions such as PFS's.

[32] Preferably, the amount of ion-extractant compound bonded (i.e., attached) to the surface of the solid support allows sufficient interaction between the ion-extractant compound and PFS's, thereby efficiently removing the PFS's from the aqueous solution. The lipophilic portion of the ion-extractant compound serves to increase the selectivity of the ion-extractant compound for PFS anions and/or interaction between the ion-extractant compound and PFS anions.

[33] In one particular embodiment of the present invention, the solid ion-extractant is a composition of formula I:



I

where each of Ar¹ and Ar² is independently C₄-C₂₀ aryl; M is a transition metal; R¹ is C₂-C₂₀ alkylene; each of X¹, X² and X³ is independently a bond, O, S, or NR⁴; each of R², R³ and R⁴ is independently H, or C₁-C₆ alkyl; Z is a solid support; Y is an anion; and a is 0 when the extractant compound is deactivated (i.e., reduced), and a is an integer from 1 to 3 when the extractant compound is activated (i.e., oxidized). Alternatively, -X²R² and/or -X³R³ can be halide, preferably chloride.

[34] Alkyl groups according to the present invention are aliphatic hydrocarbons which can be straight or branched chain groups. Alkyl groups optionally can be substituted with one or more substituents, such as a halogen, alkenyl, alkynyl, aryl, hydroxy, amino, thio, alkoxy, carboxy, oxo or cycloalkyl. There may be optionally inserted along the alkyl group one or more oxygen, sulfur or substituted or unsubstituted nitrogen atoms. Exemplary alkyl groups include methyl, ethyl, *i*-propyl, *n*-butyl, *t*-butyl, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, trichloromethyl, and pentafluoroethyl.

[35] "Aryl" groups are monocyclic or bicyclic carbocyclic or heterocyclic aromatic ring moieties. Aryl groups can be substituted with one or more substituents, such as a halogen, alkenyl, alkyl, alkynyl, hydroxy, amino, thio, alkoxy or cycloalkyl. Exemplary aryl groups include pyrrole, thiophene, furan, imidazole, pyrazole, 1,2,4-triazole, pyridine, pyrazine, pyrimidine, pyridazine, thiazole, isothiazole, oxazole, isoxazole, *s*-triazine, benzene, indene, isoindene, benzofuran, dihydrobenzofuran, benzothiophene, indole, 1H-indazole, indoline, azulene, tetrahydroazulene, benzopyrazole, benzoxazole, benzoimidazole, benzothiazole, 1,3-benzodioxole, 1,4-benzodioxan, purine, naphthalene, tetralin, coumarin, chromone, chromene, 1,2-dihydrobenzothiopyran, tetrahydrobenzothiopyran, quinoline, isoquinoline, quinazoline, pyrido[3,4-*b*]-pyridine, and 1,4-benisoaxazine.

[36] With respect to the above compound I:

[37] Preferably M is Fe, Ru, Mn, Co, Ni, Cr, Os, Rh or Ir. More preferably, M is Fe or Ru.

[38] Preferably R¹ is C₂-C₁₂ alkylene, more preferably C₂-C₈ alkylene, still more preferably C₂-C₆ alkylene, and most preferably 2-methyl hexylene or ethylene.

[39] Preferably Ar¹ and Ar² are independently cyclopentadienyl, dicarbollide or phenyl, each of which can be optionally substituted.

[40] Preferably, X¹, X² and X³ are O.

[41] Preferably, R² and R³ are C₁-C₆ alkyl. More preferably R² and R³ are independently methyl, ethyl, isopropyl, butyl, or pentyl.

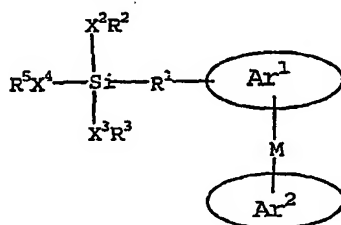
[42] Preferably, a is 1 when the extractant compound is activated, i.e., oxidized.

[43] The solid ion-extractant of formula I can be prepared by contacting the solid support of composition II:



II

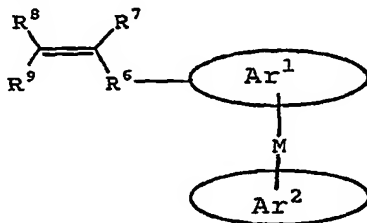
with the extractant compound of formula III:



III

where R⁵ is independently H or C₁-C₆ alkyl; X⁴ is independently a bond, O, S, or NR⁴; and Ar¹, Ar², X¹, X², X³, R¹, R², R³, R⁴, M and Z are described above. Preferably, R⁵ is H, methyl, ethyl, isopropyl or butyl. Preferably, X⁴ is O. Alternatively -X⁴R⁵ can be halide, preferably chloride.

[44] The ion-extractant compounds of formula III can be prepared by contacting an olefin of formula IV:



IV

with a silane compound of formula V:



V

in the presence of a coupling catalyst, where Ar¹, Ar², X¹, X², X³, R¹, R², R³, R⁴, M, Z, R⁵ and X⁴ are described above; R⁶ is a bond or C₁-C₁₈ alkylene; and each of R⁷, R⁸ and R⁹ is independently H or C₁-C₆ alkyl. Preferably, R⁶ is a bond or C₁-C₆ alkylene. More preferably R⁶ is a bond or methylene (-CH₂-). Preferably, R⁷, R⁸ and R⁹ are H or methyl (-CH₃).

[45] Exemplary coupling catalysts useful for producing ion-extractant compound III from the corresponding olefin IV and silyl compound V are shown in Figure 2. Preferably, the coupling catalyst is selected from the group consisting of Karstedt's catalyst, Speier's catalyst, other silylplatinum complexes, transition metal nanoclusters, dicobalt

octacarbonyl, nickel tetracarbonyl, Wilkinson's catalyst, chromium hexacarbonyl, and zirconocenes.

[46] The olefin compounds IV of the present invention can be synthesized from readily available starting materials. Various substituents on the aryl groups Ar¹ and Ar² can be present in the starting compounds, added to any one of the intermediates or added after formation of the final products by known methods of substitution or conversion reactions. If the substituents themselves are reactive, then the substituents can themselves be protected according to the techniques known in the art. A variety of protecting groups are known in the art, and can be employed. Examples of many of the possible groups can be found in *Protective Groups in Organic Synthesis*, 2nd edition, T.H. Greene and P.G.M. Wuts, John Wiley & Sons, New York, 1991, which is incorporated by reference herein in its entirety. For example, nitro groups can be added by nitration and the nitro group can be converted to other groups, such as amino by reduction, and halogen by diazotization of the amino group and replacement of the diazo group with halogen. Acyl groups can be added by Friedel-Crafts acylation. The acyl groups can then be transformed to the corresponding alkyl groups by various methods, including the Wolff-Kishner reduction and Clemmenson reduction. Amino groups can be alkylated to form mono- and di-alkylamino groups; and mercapto and hydroxy groups can be alkylated to form corresponding ethers. Primary alcohols can be oxidized by oxidizing agents known in the art to form carboxylic acids or aldehydes, and secondary alcohols can be oxidized to form ketones. Thus, substitution or alteration reactions can be employed to provide a variety of substituents throughout the molecule of the starting material, intermediates, or the final product, including isolated products.

[47] Since the compounds of the present invention can have certain substituents which are necessarily present, the introduction of each substituent is, of course, dependent on the specific substituents involved and the chemistry necessary for their formation. Thus, consideration of how one substituent would be affected by a chemical reaction when forming a second substituent would involve techniques familiar to one of ordinary skill in the art. This would further be dependent on the aryl ring involved.

[48] It is to be understood that the scope of this invention encompasses not only the various isomers which may exist but also the various mixture of isomers which may be formed.

[49] When the compound of the present invention contains an olefin moiety and such olefin moiety can be either cis- or trans-configuration, the compound can be

synthesized to produce cis- or trans-olefin, selectively, as the predominant product.

Alternatively, the compound containing an olefin moiety can be produced as a mixture of cis- and trans-olefins and separated using known procedures, for example, by chromatography as described in W.K. Chan, et al., *J. Am. Chem. Soc.*, 1974, 96, 3642, which is incorporated by reference herein in its entirety.

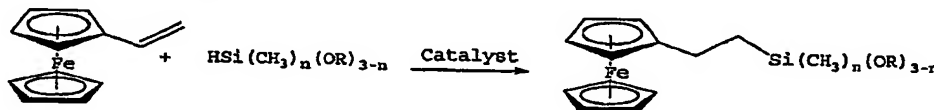
[50] Additional objects, advantages, and novel features of this invention will become apparent to those skilled in the art upon examination of the following examples thereof, which are not intended to be limiting.

EXPERIMENTAL

Experiment 1

[51] This experiment illustrates a method for coupling a silane compound to vinylferrocene.

[52] A variety of silane compounds were coupled to vinylferrocene using different catalysts as shown below:



Some of the results are shown on Table 1.

Table 1. Vinylferrocene Hydrosilylation Results

Silane	catalyst ^a	amt. of catalyst ^b	% yield ^c
HSiCl_3	Karstedt's	0.08% to 1.6%	no rxn.
$\text{HSi}(\text{CH}_3)_2(\text{OEt})$	Karstedt's	0.24%	67%
$\text{HSi}(\text{CH}_3)(\text{OEt})_2$	no catalyst	0	no rxn.
$\text{HSi}(\text{OEt})_3$	Karstedt's	0.40%	27%
$\text{HSi}(\text{OEt})_3$	Speier's	0.02%	17%
$\text{HSi}(\text{OMe})_3$	Karstedt's	0.16% to 1.6%	<1% ^d

- a. Karstedt's catalyst was purchased as a 2-3% platinum solution (by weight) in xylenes from United Chemical Technologies, Inc. (Bristol, PA) and was assumed to be 2.5% platinum with a solution density of 0.88 g/mL; Speier's catalyst was purchased from Aldrich (Milwaukee, WI) and dissolved in 2-propanol and used as a 0.01 M solution.
- b. Values are expressed as mole percent platinum relative to the starting amount of vinylferrocene.
- c. Percent yields given are approximate. Final products still contain minor amounts of impurities.
- d. Product observed in mass spectrometry.

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[53] As shown in Table 1, the presence of electron withdrawing groups on the silane starting material affects the yield of hydrosilylation reaction. For example, no silylated ferrocene was observed for the reaction with HSiCl_3 , which has three electron withdrawing chlorine atoms bonded to the silicon atom. The more electron withdrawing groups bonded to the silicon atom, the stronger the Si-H bond becomes and the more difficult it is to add the Si-H moiety across a double bond. This trend can also be seen in the lower yield obtained for the trialkoxysilanes compared to the monoalkoxysilane. The electron withdrawing alkoxy substituents strengthen the Si-H bond while electron donating alkyl groups weaken it.

[54] The hydrosilylation reaction with the dialkylmonoalkoxy silane $\text{HSi}(\text{CH}_3)_2(\text{OEt})$ produced a greater yield of hydrosilylated product than trialkoxysilane $\text{HSi}(\text{OEt})_3$. In addition, the alkyl substituent of the alkoxy group also affect the product yield. Compare for example, the result between trimethoxysilane and triethoxysilane. Without being bound by a theory, it is believed that the more electron density the oxygen atom receives from the alkyl group, the less electron density it will take from the silicon atom; thus, it is believed that the added electron donating ability of an ethyl group over a methyl group is responsible for the difference in product yield. The overall effect of substituting ethoxy for methoxy groups is to weaken the Si-H bond and make the hydrosilylation reaction more favorable.

Experiment 2

[55] This experiment illustrates the solubility of PFS salts at a different water temperatures.

[56] A 57 mg sample of FC-95 (a mixture of five potassium salts of PFS anions) from 3M company (St. Paul, Minnesota) was mixed with 30 mL of water at 23 °C. After vigorous mixing, the mixture contained a saturated solution of FC-95 and a considerable amount of solid FC-95. The mixture was heated to 80 °C, whereupon all of the solids dissolved. The mixture was then cooled to about 0 °C, whereupon white crystals precipitated. The mixture was filtered cold and the crystals were dried to yield 32 mg of solid. The filtrate was concentrated in vacuum to yield 25 mg of white solid.

Experiment 3

[57] This experiment illustrates the thermal stabilities of 1,1'3,3'-tetrakis(2-methyl-2-hexyl)ferrocene (HEP) and 1,1'3,3'-tetrakis(2-methyl-2-hexyl)ferricenium cation (HEP^+).

[58] A samples of HEP and $\text{HEP}^+\text{NO}_3^-$ were added to water and the resulting mixture was heated to 80 °C for several days. There was no visible degradation of either material when compared with control samples treated with water at 23 °C for the same length of time.

5 Experiment 4

[59] This experiment illustrates a method for attaching ferrocenes to indium tin oxide (ITO) surfaces.

[60] The ITO coated glass slide was hydroxylated by soaking in a 0.5 M aqueous solution of KOH for 24 hours. The hydroxylated ITO slide was placed in a benzene solution of 1-(2'-triethoxysilylethyl) ferrocene for 24 hours. The slide was then rinsed with benzene and analyzed by cyclic voltammetry, which showed the ferrocene to be attached to the slide.

Experiment 5

[61] This experiment shows efficiency of the PFS anion recovery process of the present invention.

[62] AFFF (FC-203CF Light Water Brand 3% solution from 3M Company) concentrate contains five different PFS anions, C_4 through C_8 PFS anions. The PFS-8, i.e., C_8 PFS, component is about 71 mole%, and its concentration is about 10.9 mM. For the sake of convenience, the following calculations assume PFS-8 is the only PFS anion in AFFF.

[63] The nominal concentration, representing all of the PFS anions, is about 15 mM (10.9/0.71). The wastewater containing AFFF is at most about 3% solution of the concentrate, since this is the standard dilution used to spray on liquid-fuel fires. Therefore, the nominal concentration of PFS-8 in the wastewater is at most about 0.45 mM (about 218 ppm). A typical 16 gallon recovery column 10 holds about 8 Kg of $\text{HEP}^+\text{NO}_3^-/\text{XAD-7}$ (acrylic ester polymer available from Supelco®) with an ion-exchange capacity of about 0.24 mmol/g and a void volume of about 2 gallons (about 8 L). Therefore, the ion-exchange capacity of the column is about 2 mole of PFS-8, or about 880 g of potassium PFS-8.

[64] The flow rate through the column used is about 7 gal/min (or about 3.5 times the void volume per minute). Therefore, about 800 gallons of 0.45 mM PFS-8 solution can be treated during 1.9 hours, resulting in about 1% of PFS-8 being unrecovered (about 2 ppm, well below the 10 ppm foaming level). At this point about 37% of the ion-exchange sites are saturated, i.e., about 325 g of PFS-8 is contained in the column 10.

[65] The solubility of potassium PFS-8 (*i.e.*, KPFS-8) is about 1 g/L or less at 23 °C. Therefore, when 1 equiv. of void volume (*i.e.*, 2 L) of deactivation solution flows through the column 10, the resulting effluent will contain only about 8 g of the 325 g of "released" (*e.g.*, precipitated) KPFS-8.

[66] After the deactivating solution is removed from the column 10, the remaining KPFS-8 is recovered using the hot water/cold water process as described above. Thus, starting from about 3200 L (*i.e.*, about 800 gallons) of wastewater, about 0.2 L of crystalline KPFS-8 can be recovered as a solid. This represents a volume reduction by factor of about 15,000.

10 Experiment 6

[67] This experiment shows efficiency of the PFS anion recovery process of the present invention.

[68] A column having 2.5 cm (diameter) and 10 cm (length) was filled with about 10.0 g of HEP⁺NO₃⁻/XAD-7 having about 0.248 mmol HEP⁺NO₃⁻ per gram of material.

[69] A saturated solution of FC-95 was made by dissolving 2.5 g of powdered FC-95 in 2 L of heated distilled and deionized water. The solution was allowed to cool to room temperature at which point precipitate was observed due to the decrease in solubility of PFS anions in cooler water. The solution was filtered through #4 Whatman filter paper to remove the precipitate. About 1.5 L of filtrate was pumped through the above column at a rate of about 3.5 mL/min.

[70] The column was then washed with water to removed the excess FC-95 solution. The ion-exchange compound was deactivated by passing a basic solution of Na₂S₂O₄ through the column. Once the deactivation solution had passed through the column, it was diverted through a cold trap (chiller) in order to collect PFS anions that might have dissolved in the solution.

[71] Hot water (96 °C) was then pumped through the column. The hot water was then passed through a cold trap. After 15 minutes a white solid was observed in the cold trap. The cold trap was washed and the white solid was dissolved in water. This final solution of PFS salts was analyzed by NIEMS using 4:1 (v/v) acetonitrile/water. The saturated solutions of FC-95, both before and after extraction, were also analyzed by NIEMS.

[72] Figure 2 shows the differences in PFS anion peak intensities for the FC-95 solution before and after passing through the column. More than 1/2 of the PFS-8 and PFS-7 in the original solution have been extracted by the column.

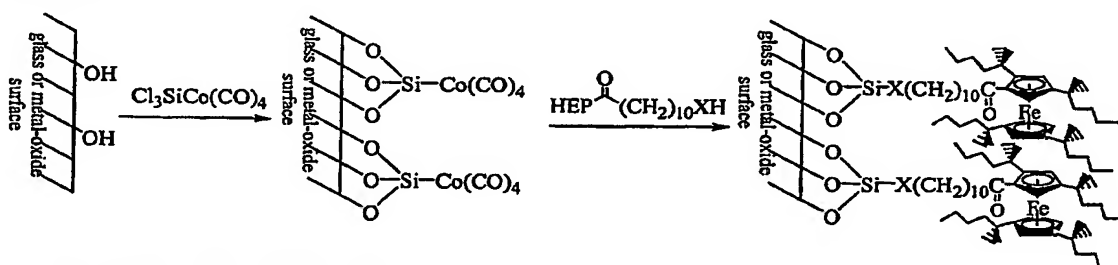
[73] Without being bound by any theory, it is believed that the more weakly hydrated the PFS anion, the larger the equilibrium constant for ion-exchange with the ion-extractant. Therefore, longer-chain PFS anions is extracted preferentially over shorter-chain PFS anions because longer-chain PFS anions have lower hydration energies than shorter-chain PFS anions.

[74] Figure 3 shows the NIEMS intensities of the PFS anions collected as their potassium salts in the cold trap. PFS-8 is the most abundant anion found in the cold trap. The concentration of PFS-7 in the cold-trap sample is significantly greater than the intensity of PFS-6 relative to a sample of the FC-95 starting material, in which the concentration ratio of PFS-7 to PFS-6 is about 0.25, even though a greater absolute amount of PFS-6 was extracted relative to PFS-7, *i.e.*, the difference between the before and after intensities for PFS-6 in Figure 2 is greater than the difference for PFS-7.

[75] The present invention, in various embodiments, includes components, methods, processes, systems and/or apparatus substantially as depicted and described herein, including various embodiments, subcombinations, and subsets thereof. Those of skill in the art will understand how to make and use the present invention after understanding the present disclosure. The present invention, in various embodiments, includes providing devices and processes in the absence of items not depicted and/or described herein or in various embodiments hereof, including in the absence of such items as may have been used in previous devices or processes, *e.g.*, for improving performance, achieving ease and/or reducing cost of implementation.

Experiment 7

[76] This example illustrates a method for attaching HEP to a glass or metal surface.



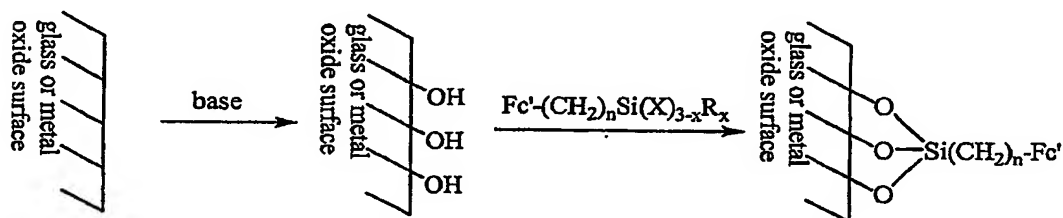
X = -O-, -S-, -COO-, -CONH-, -NH-

[77] A procedure similar to those disclosed by Kaimin et al., *Langmuir* 1992, 8, 2585; Herr et al., *J. Amer. Chem. Soc.* 1994, 116, 1157; and Mirkin et al., US Patent # 5,286,571 was used. The procedure generally involves cleaning a glass or metal-oxide

surface by hydroxylating it by soaking in a 0.5 to 1.5 M base (KOH or NaOH) in a 1:1 (v:v) H₂O:Ethanol solution for 1 to 24 hours and then rinsing successively with hot distilled water and ethanol. The surface was dried under vacuum. The surface was then soaked in a 0.01 M solution of (CH₃)_xCl_{3-x}SiCo(CO)₄ (x= 0-2) for 24 hours at room temperature under an inert atmosphere. The surface was then soaked in a 0.01 M solution of HEP-CO-(CH₂)_n-X (where X= -OH, -SH, -COOH, -NH₂, -CONH₂) in an appropriate solvent (acetonitrile or dichloromethane) for 24 to 48 hours. The surface was then rinsed with acetonitrile and dichloromethane.

Experiment 8

[78] This example illustrates another method for attaching HEP to a glass or metal surface.



Fc' = HEP or ferrocene; n = 1-12; X = alkoxy or cloro; R = alkyl; x = 0-2

[79] A clean glass or metal-oxide surface was hydroxylated by soaking in a 0.5 to 1.5 M base (KOH or NaOH) in a 1:1 (v:v) H₂O:Ethanol solution for 1 to 24 hours and then rinsing successively with hot distilled water and ethanol and drying under N₂ gas. The slide was then placed in a 0.01M solution of Fc'-(CH₂)_nSi(X)_{3-x}R_x in an appropriate solvent (ethanol, toluene, acetonitrile or dichloromethane) for 24 to 48 hours. The surface was then rinsed with acetonitrile and dichloromethane.

[80] The foregoing discussion of the invention has been presented for purposes of illustration and description. The foregoing is not intended to limit the invention to the form or forms disclosed herein. Although the description of the invention has included description of one or more embodiments and certain variations and modifications, other variations and modifications are within the scope of the invention, *e.g.*, as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative embodiments to the extent permitted, including alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures,

functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter.

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WHAT IS CLAIMED IS:

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1 1. A method for removing and recovering an ion from a solution
2 comprising:
3 (a) contacting said solution with a solid ion extractant comprising an
4 activated ion coordinating agent to remove at least a portion of said ion from said solution;
5 (b) deactivating said ion coordinating agent;
6 (c) dissolving said ion in a recovery solvent and removing said ion from
7 said solid ion extractant; and
8 (d) recovering said ion from said recovery solvent.

1 2. The method of Claim 1, wherein said ion is an anion.

1 3. The method of Claim 1, wherein said ion is a perfluoroalkylsulfonate
2 or a perfluoroalkyl carboxylate.

1 4. The method of Claim 1, wherein said ion coordinating agent comprises
2 a lipophilic portion.

1 5. The method of Claim 1, wherein said active ion coordinating agent is
2 ionizable in an aqueous solution.

1 6. The method of Claim 1, wherein said step of removing said ion from
2 said solution comprises an ion-exchange process.

1 7. The method of Claim 1, wherein said ion coordinating agent is an
2 organometallic compound.

1 8. The method of Claim 1, wherein said ion coordinating agent is redox-
2 recyclable.

1 9. The method of Claim 8, wherein said ion coordinating agent is
2 oxidized prior to said step (a).

1 10. The method of Claim 9, wherein said oxidation step comprises an
2 electrochemical oxidation process.

1 11. The method of Claim 9, wherein said oxidation step comprises a
2 chemical oxidation process.

1 12. The method of Claim 8, wherein said deactivation step comprises
2 reducing said ion coordinating agent.

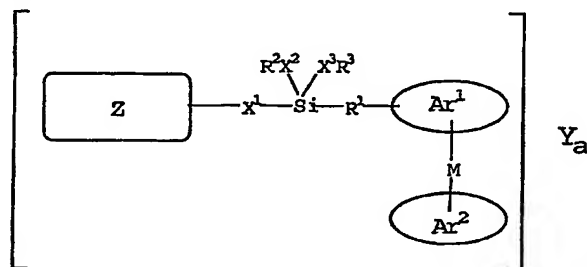
1 13. The method of Claim 12, wherein said reduction step comprises an
2 electrochemical reduction process.

1 14. The method of Claim 12, wherein said reduction step comprises a
2 chemical reduction process.

1 15. The method of Claim 14, wherein said chemical reduction process
2 comprises contacting said solid ion extractant with a deactivating solution.

1 16. The method of Claim 15, wherein said deactivating solution comprises
2 a compound selected from the group consisting of $\text{Na}_4\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{Na}_2\text{S}_2\text{O}_4$, Cr^{2+}
3 salt, V^{2+} salt and NaBH_4 .

1 17. The method of Claim 1, wherein said solid ion extractant is a
2 composition of the formula:



3
4 wherein

5 each of Ar^1 and Ar^2 is independently $\text{C}_4\text{-C}_{20}$ aryl;

6 M is a transition metal;

7 R^1 is $\text{C}_2\text{-C}_{20}$ alkylene;

8 each of X^1 , X^2 and X^3 is independently a bond, O, S, or NR^4 ;

9 each of R^2 , R^3 and R^4 is independently H, or $\text{C}_1\text{-C}_6$ alkyl;

10 Z is a solid support;

11 Y is an anion; and

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1 a is 0 when said ion coordinating agent is deactivated, and
13 a is an integer from 1 to 3 when said ion coordinating agent is activated.

1 18. The method of Claim 17, wherein M is selected from the group
2 consisting of Fe, Ru, Mn, Co, Ni, Cr, Os, Rh and Ir.

1 19. The method of Claim 17, wherein Ar¹ and Ar² are selected from the
2 group consisting of cyclopentadienyl, dicarbollide and phenyl, each of which can be
3 optionally substituted.

1 20. The method of Claim 17, wherein each of X¹, X² and X³ is
2 independently a bond or O.

1 21. The method of Claim 17, wherein R² and R³ are C₁-C₆ alkyl.

1 22. The method of Claim 17, wherein said solid support is glass or a
2 polymeric resin.

1 23. The method of Claim 22, wherein said polymeric resin is selected from
2 the group consisting of acrylic ester, polyvinyl, polystyrene, polypyrrole, polyolefin, and
3 polyaromatic.

1 24. The method of Claim 17, wherein Y is selected from the group
2 consisting of nitrate, halide, HSO₄⁻, ClO₄⁻, ReO₄⁻, PF₆⁻, carboxylate and CF₃SO₃⁻.

1 25. The method of Claim 17, wherein a is 1 when said ion coordinating
2 agent is activated.

1 26. The method of Claim 1, wherein said solution is an aqueous solution.

1 27. The method of Claim 26, wherein the temperature of solution of said
2 step (a) is least about 24 °C.

1 28. The method of Claim 1, wherein the temperature of said recovery
2 solution is at least about 85 °C.

1 (c) dissolving said anion in a recovery solvent and removing said anion
19 from said solid ion extractant; and

20 (d) recovering said anion.

1 33. The method of Claim 32, wherein said anion is a perfluoroalkyl
2 sulfonate or perfluoroalkyl carboxylate.

1 34. The method of Claim 32, wherein said step of removing said anion
2 from said aqueous solution comprises an ion-exchange process.

1 35. The method of Claim 32, wherein a in said step (a) is 1.

1 36. The method of Claim 32, wherein said ion coordinating agent is redox-
2 recyclable.

1 37. The method of Claim 36, further comprising a step of oxidizing said
2 ion coordinating agent from $a=0$ to $a=1$ prior to said step (a).

1 38. The method of Claim 37, wherein said oxidizing step comprises an
2 electrochemical oxidation process.

1 39. The method of Claim 37, wherein said oxidizing step comprises a
2 chemical oxidation process.

1 40. The method of Claim 36, wherein said deactivation step comprises
2 reducing said ion coordinating agent.

1 41. The method of Claim 40, wherein said reducing step comprises an
2 electrochemical reduction process.

1 42. The method of Claim 40, wherein said reducing step comprises a
2 chemical reduction process.

1 43. The method of Claim 42, wherein said chemical reduction process
2 comprises contacting said solid ion extractant with a deactivating solution.

1 44. The method of Claim 43, wherein said deactivating solution comprises
2 a compound selected from the group consisting of $\text{Na}_4\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{Na}_2\text{S}_2\text{O}_4$, Cr^{2+}
3 salt, V^{2+} salt and NaBH_4 .

1 45. The method of Claim 32, wherein M is selected from the group
2 consisting of Fe, Ru, Mn, Co, Ni, Cr, Os, Rh and Ir.

1 46. The method of Claim 45, wherein Ar¹ and Ar² are selected from the
2 group consisting of cyclopentadienyl, dicarbollide and phenyl, each of which can be
3 optionally substituted.

1 47. The method of Claim 46, wherein each of X¹, X² and X³ is
2 independently a bond or O.

1 48. The method of Claim 47, wherein R² and R³ are C₁-C₆ alkyl.

1 49. The method of Claim 48, wherein said solid support is glass or a
2 polymeric resin.

1 50. The method of Claim 49, wherein said polymeric resin is selected from
2 the group consisting of acrylic ester, polyvinyl, polystyrene, polypyrrole, polyolefin, and
3 polyaromatic.

1 51. The method of Claim 50, wherein Y is selected from the group
2 consisting of nitrate, halide, HSO₄⁻, ClO₄⁻, ReO₄⁻, PF₆⁻, carboxylate and CF₃SO₃⁻.

1 52. The method of Claim 32, wherein the temperature of said aqueous
2 solution of said step (a) is least about 24 °C.

1 53. The method of Claim 52, wherein the temperature of said recovery
2 solution is at least about 85 °C.

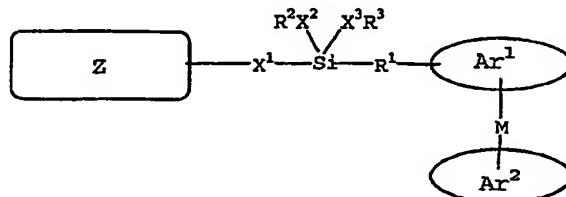
1 54. The method of Claim 53, wherein said recovery step (d) comprises
2 reducing the temperature of said recovery solution to less than about 5 °C to precipitate said
3 anion.

1 55. The method of Claim 54, wherein said recovery step further comprises
2 separating said precipitated ion from said recovery solution.

1 56. The method of Claim 32, further comprising:
2 (e) re-activating said deactivated ion coordinating agent; and

(f) repeating said steps (a)-(e).

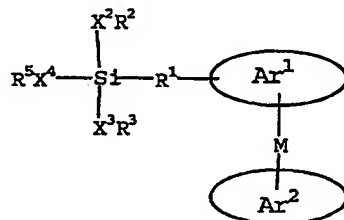
57. A process for producing a solid ion extractant composition of the formula:



said process comprising contacting the solid support of the composition:



with an ion coordinating agent of the formula:



wherein

each of Ar^1 and Ar^2 is independently C_4 - C_{20} aryl;

each of X^1 , X^2 , X^3 and X^4 is independently a bond, O, S, or NR^4 ;

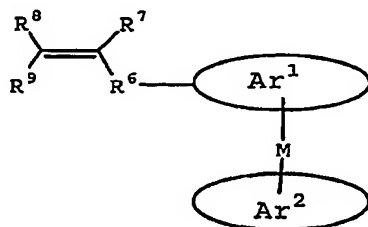
R^1 is C_2 - C_{20} alkylene;

each of R^2 , R^3 , R^4 and R^5 is independently H, or C_1 - C_6 alkyl;

M is a transition metal; and

Z is a solid support.

58. The process of Claim 57, further comprising the step of producing said ion coordinating agent, wherein said ion coordinating agent producing step comprises contacting an olefin of the formula:



with a silyl compound of the formula $\text{HSi}(\text{X}^2\text{R}^2)(\text{X}^3\text{R}^3)(\text{X}^4\text{R}^5)$ in the presence of a catalyst to
produce said ion coordinating agent,
wherein

R^6 is a bond or $\text{C}_1\text{-C}_{18}$ alkylene; and
each of R^7 , R^8 and R^9 is independently H or $\text{C}_1\text{-C}_6$ alkyl.

59. The method of Claim 58, wherein said catalyst is selected from the
group consisting of Karstedt's catalyst, Speier's catalyst, other silylplatinum complexes,
transition metal nanoclusters, dicobalt octacarbonyl, nickel tetracarbonyl, Wilkinson's
catalyst, chromium hexacarbonyl, and zirconocenes.

60. The process of Claim 57, wherein M is selected from the group
consisting of Fe, Ru, Mn, Co, Ni, Cr, Os, Rh and Ir.

61. The process of Claim 60, wherein Ar^1 and Ar^2 are selected from the
group consisting of cyclopentadienyl, dicarbollide and phenyl, each of which can be
optionally substituted.

62. The process of Claim 61, wherein each of X^1 , X^2 and X^3 are
independently a bond or O.

63. The process of Claim 62, wherein X^4 is O.

64. The process of Claim 63, wherein R^2 , R^3 and R^5 are $\text{C}_1\text{-C}_6$ alkyl.

65. The process of Claim 64, wherein said solid support is glass or a
polymeric resin.

66. The process of Claim 65, wherein said polymeric resin is selected from
the group consisting of acrylic ester, polyvinyl, polystyrene, polypyrrole, polyolefin, and
polyaromatic.

67. The process of Claim 57, further comprising oxidizing said solid ion
extractant to produce an activated solid ion extractant of the formula:

R¹ is C₂-C₂₀ alkylene;

each of R², R³, R⁴ and R⁵ is independently H, or C₁-C₆ alkyl; and

M is a transition metal.

75. The compound of Claim 74, wherein M is selected from the group consisting of Fe, Ru, Mn, Co, Ni, Cr, Os, Rh and Ir.

76. The compound of Claim 74, wherein Ar¹ and Ar² are selected from the group consisting of cyclopentadienyl, dicarbollide and phenyl, each of which can be optionally substituted.

77. The compound of Claim 74, wherein each of X¹, X², X³ and X⁴ is independently a bond or O.

78. The compound of Claim 74, wherein R² and R³ are C₁-C₆ alkyl.

ABSTRACT OF THE DISCLOSURE

The present invention provides solid ion-extractant and a method for using the same in extracting and recovering ions in a solution. In particular, the present invention provides a method for extracting and recovering ions which are relatively insoluble in a solvent at a particular solvent temperature range. More specifically, the present invention provides a method for extracting and recovering perfluoroalkylsulfonates from an aqueous solution.

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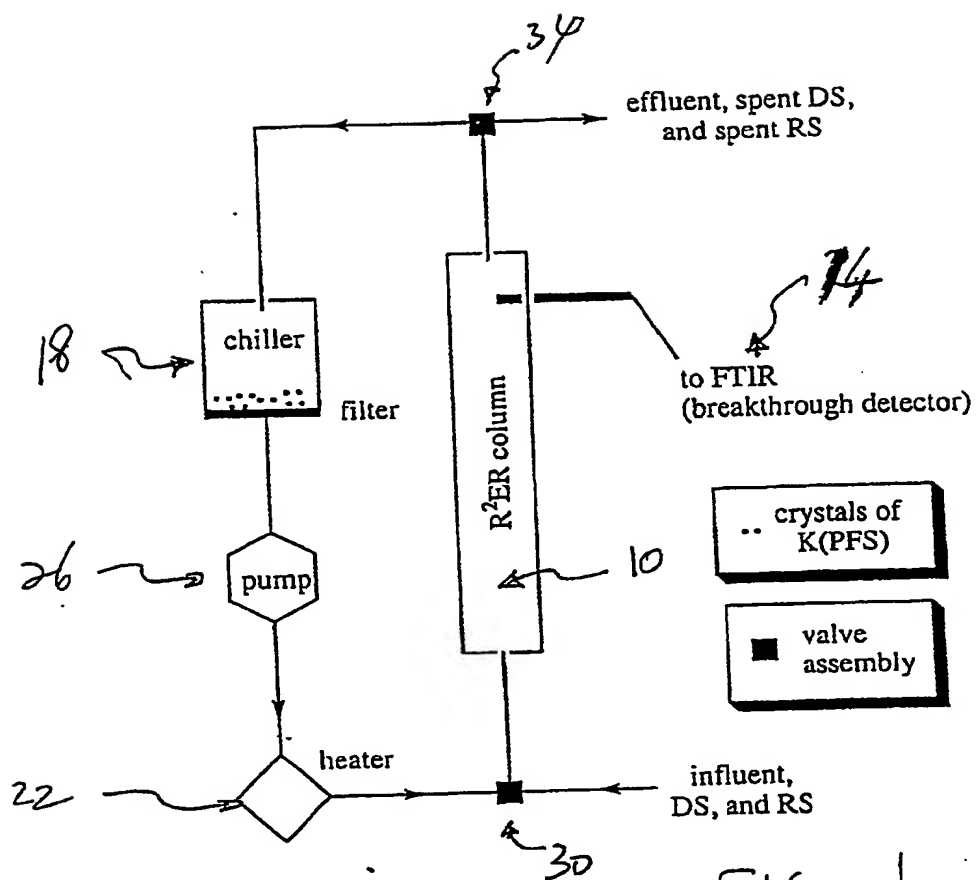
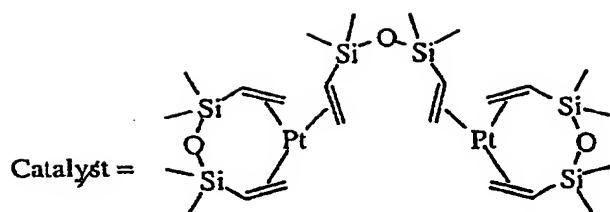
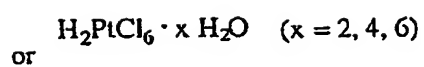


FIG. 1



Karstedt's Catalyst



Speier's Catalyst

Fig. 2

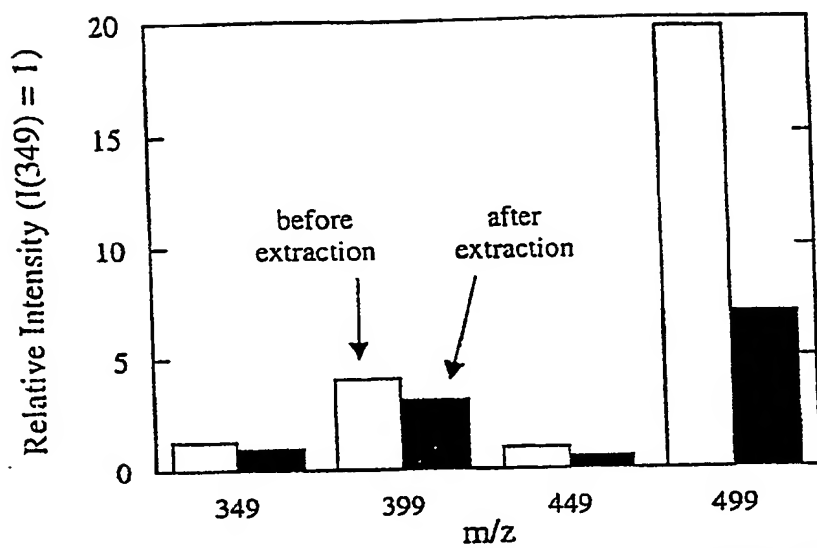


Figure 3 Concentration of PFS anions before and after extraction with $\text{HEP}^+\text{NO}_3^-/\text{XAD-7}$. The error bars represent $\pm 3\sigma$. The m/z values for PFS-5, PFS-6, PFS-7, and PFS-8 are 349, 399, 449 and 499, respectively (PFS-8 = $\text{C}_8\text{F}_{17}\text{SO}_3^-$).

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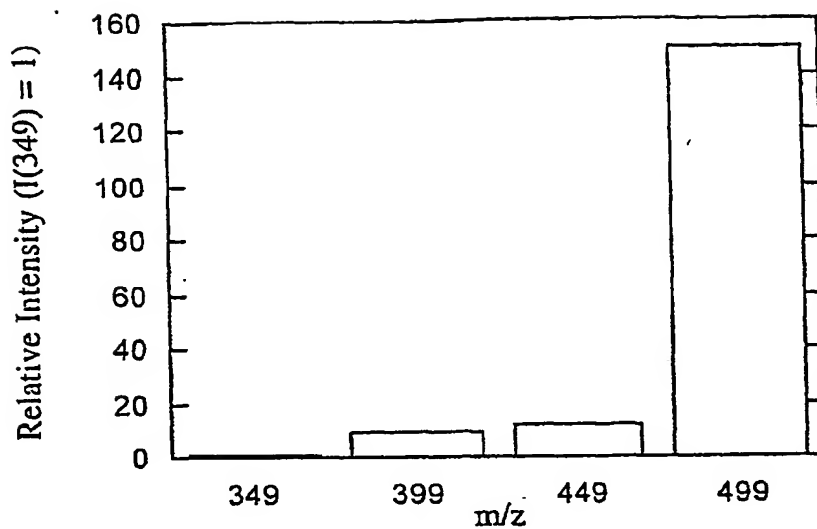


Figure 4. Relative NIEMS intensities of PFS anions found in cold trap. Note that the intensity, and hence the concentration, of PFS-7 in the cold-trap sample is much greater than the intensity of PFS-6 relative to a sample of the FC-95 starting material, in which the concentration ratio PFS-7/PFS-6 is approximately 0.25.

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Detection of Ions in a Fluid Medium

FIELD OF THE INVENTION

5 The present invention is directed to a method and apparatus for detecting a presence of an ion in a fluid medium.

BACKGROUND OF THE INVENTION

10 The ability to detect a presence of, or to quantify the amount of, a pollutant in a solution is generally limited by the concentration of the pollutant and the sensitivity of the method utilized.

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15 One of the useful tools for determining the presence of trace contaminants in a variety of samples is infrared (i.e., IR) spectroscopy. However, the usefulness of IR spectroscopy for water samples has been limited due to water's strong absorbance of electromagnetic radiation in the infrared region. This problem can be mitigated by using waveguide sampling (i.e., attenuated total reflection or ATR) IR spectroscopy, which allows aqueous systems to be monitored via IR spectroscopy. Unfortunately, the detection limits for current ATR IR spectroscopy are inadequate for determining trace amounts of contaminants. Typically, detection limits are constrained due to absorption of IR radiation by water and the small volume of solution probed by the evanescent wave
20 that propagates out of the waveguide (i.e., the ATR crystal) into the solution.

25 A number of methods have been developed to decrease the detection limit in ATR sampling for organic compounds, such as pesticides and insecticides, by coating the waveguide surface with a thin film which is designed to interact with organic compounds (e.g., typically by hydrophobic interactions). It is believed that this interaction between the thin film and an organic compound increases the net concentration of the organic compound in the region sampled by the evanescent wave, thereby effectively reducing the detection limit of ATR IR spectroscopy.

30 Unfortunately, these films are not applicable to detecting ionic pollutants, including weakly-hydrated ions, in aqueous solutions. Moreover, currently used thin films for ATR IR spectroscopy require time consuming processes to reactivate the films after each use, i.e., none of the thin films currently used in ATR IR spectroscopy is capable of being rapidly deactivated and reactivated for detecting pollutants again and again without loss of performance.

Therefore, there is a need for rapidly detecting ionic pollutants in aqueous solutions. There is also a need for a thin film which is useful in ATR IR spectroscopy and which can be rapidly deactivated and reactivated for detecting ionic pollutants.

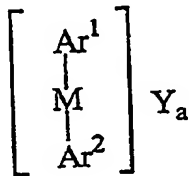
SUMMARY OF THE INVENTION

The present invention provides a detection probe which provides a higher concentration of an ion on the detection probe relative to the concentration of the ion in a fluid medium and a method for using the same.

The detection probe comprises an extractant compound which has a higher affinity for the ion than the fluid medium. Preferably, the extractant compound forms a thin film coating on a surface of the detection probe. The thin film can be temporarily or permanently attached to the detection probe. In addition, the thin film can also include a linker which is used to attach the extractant compound to the detection probe. In one particular embodiment of the present invention, the extractant compound is covalently bonded to a surface of the detection probe.

Preferably, the extractant compound is an organometallic compound which is redox-recyclable. In this manner, oxidation of the extractant compound results in the extractant compound which is cationic and therefore requires the presence of an anionic counterion in the extractant coating. When the ionizable extractant compound is contacted with the fluid medium containing the target anion, anion ion exchange occurs leading to a higher local concentration of the target anion on the detection probe relative to the concentration of the target anion in the fluid medium. The extractant compound can be activated and deactivated (i.e., oxidized and reduced, respectively) electrochemically or by using inexpensive redox agents. Deactivation of the extractant compound results in a neutral form of the extractant compound which releases the target anion from the extractant coating on the detection probe.

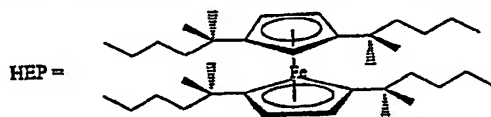
In one particular embodiment of the present invention, the extractant compound is of the formula:



I

where each of Ar^1 and Ar^2 is independently optionally substituted C_4 - C_{20} aryl; preferably each of Ar^1 and Ar^2 is independently alkyl substituted cyclopentadienyl, or indenyl. M is a transition metal, preferably Fe, Co, or Ni. Y is an anion, preferably nitrate, or chloride. And a is 0 when the extractant compound is deactivated (e.g., reduced), and a is an integer from 1 to 3, preferably 1, when the extractant compound is activated (e.g., oxidized).

In one embodiment of the present invention, the extractant compound is selected from the group consisting of 1,1',3,3'-tetrakis(2-methyl-2-hexyl)ferricenium nitrate (i.e., $HEP^+NO_3^-$), 1,1',3,3'-tetrakis(2-methyl-2-hexyl)ferricenium chloride (i.e., HEP^+Cl^-), 1,1',3,3'-tetrakis(2-methyl-2-nonyl)ferricenium nitrate (i.e., $DEC^+NO_3^-$) and 1,1',3,3'-tetrakis(2-methyl-2-nonyl)ferricenium chloride (i.e., DEC^+Cl^-).



The detection probes of the present invention can be IR spectroscopy detection probes or electrochemical probes which measure electric conductivity, resistivity, capacity, or current as a function of potential. Preferably, IR spectroscopy detection probes are attenuated total reflection IR spectroscopy probes, i.e., ATR IR sensing elements.

The detection probes of the present invention are well suited for qualitative and/or quantitative analysis of weakly-hydrated ions. Preferably, ions are selected from the group consisting of perfluoroalkylsulfonates, alkylsulfates, carborane monoanions, tetrafluoroborate, hexafluorophosphate, perchlorate, pertechnetate, perhenate, cyanide, cyanate, thiocyanate, monoalkyl esters of deprotonated alkylphosphonic acids, bisulfate, and penicillin-G.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an IR spectrum of an aqueous solution of 1 mM $Li^+CF_3SO_3^-$ using an unmodified (i.e., without any extractant compound), SiComp[®] (silicon) attenuated total reflectance (ATR) sensing element; and

Fig. 2 is an IR spectrum of an aqueous solution of 1 mM $Li^+CF_3SO_3^-$ using a modified (i.e., with $HEP^+NO_3^-$ as an extractant compound), SiComp[®] (silicon) attenuated total reflectance (ATR) sensing element.

DETAILED DESCRIPTION OF THE INVENTION

“Aryl” means a monovalent monocyclic or bicyclic aromatic hydrocarbon radical which is optionally substituted independently with one or more substituents, preferably one, two or three, substituents. Preferred substituents include alkyl, amino, and phosphino moieties. More specifically the term aryl includes, but is not limited to, cyclopentadienyl, indenyl, phenyl, and the like, and the derivatives thereof.

“Alkyl” means a linear or branched saturated monovalent hydrocarbon radical of one to twenty carbon atoms, e.g., methyl, ethyl, propyl, 2-propyl, *n*-butyl, *iso*-butyl, *tert*-butyl, pentyl, hexyl, 2-methylhexyl, 2-methylnonyl, and the like.

Unless the context requires otherwise, the term “coated” refers to attachment of an extractant compound to a detection probe by any physical or chemical means. Therefore, coating can include attachment of the extractant compound and the detection probe through a covalent or ionic bond formation; hydrophilic, hydrophobic or Van der Waals force interaction between the extractant compound and the detection probe; as well as any other known methods including coating a polymer containing the extractant compound onto the detection probe or generating a sol-gel-derived material containing the extractant compound.

The present invention provides a method and a device for detecting a presence of, or quantifying the amount of, an ion in a fluid medium. As used in this invention, a “fluid medium” refers to a gas or a liquid, preferably a liquid, and more preferably an aqueous solution. In particular, the present invention is directed to increasing the relative concentration of the ion near the surface of a detection probe ATR crystal relative to the concentration of the ion in the fluid medium. In this manner, the sensitivity of the detection probe is greatly increased; thus, allowing qualitative and/or quantitative analysis of the ion in the fluid medium.

As used herein, a “detection probe” refers to a device which is used for detecting or sensing (*i.e.*, a device which sends back information regarding) the presence or quantity of the ion in a fluid medium. Thus, a detecting probe is a device which sends and/or receives information to and from the fluid medium. Alternatively, a detecting probe may comprise two separate units in which one of the units is used to send information to the fluid medium and the other is used to receive information from the fluid medium.

The detection probes of the present invention detect a variety of signals including electromagnetic waves, such as radio waves, infrared waves, visible waves and

ultraviolet waves; electric signals, such as conductivity, capacity and resistivity; and electrical current as a function of electrical potential. Preferably, detection probes of the present invention detect infrared waves, electrical current as a function of electrical potential, or electronic conductivity.

5 Detection probes of the present invention can be used to determine the presence of, or to quantify the amount of, a variety of ions, particularly, weakly-hydrated ions. As used herein, a "weakly-hydrated ion" refers to an ion with an enthalpy of hydration less negative than that of the nitrate anion. Exemplary weakly-hydrated ions include ions containing a lipophilic moiety such as hydrocarbylsulfonates, for example, 10 perfluoroalkylsulfonates (e.g., $C_nF_{2n+1}SO_3^-$); hydrocarbylsulfates, hydrocarbylphosphates; hydrocarbylphosphonates; and hydrocarbylcarboxylates; As used herein, a "hydrocarbyl" refers to a hydrocarbon compound or a moiety which can be straight, a branched chain group or a ring. Hydrocarbyls optionally can be substituted with one or more substituents, such as a halogen, alkenyl, alkynyl, aryl, hydroxy, amino, thio, alkoxy, 15 carboxy, oxo or cycloalkyl. There may be optionally inserted along the alkyl group one or more oxygen, sulfur or substituted or unsubstituted nitrogen atoms. Exemplary hydrocarbyls include methyl, ethyl, *i*-propyl, *n*-butyl, *t*-butyl, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, trichloromethyl, and pentafluoroethyl.

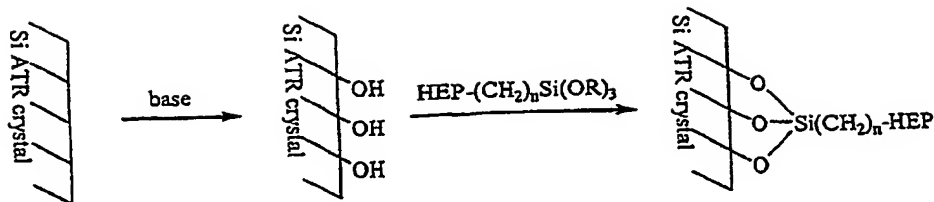
Particular aspects of the present invention will now be described in the 20 context of attenuated total reflection Fourier-transform infrared (ATR FT-IR) sensing element, i.e., waveguide or detection probe, for detecting the presence of, or the quantity of, perfluoroalkylsulfonate anions (PFS anions) in an aqueous solution. Such descriptions are not intended to limit the general applicability of the present invention to only detecting PFS anions in an aqueous solution using ATR FT-IR.

25 A quantitative or qualitative analysis of PFS anions in an aqueous solution can be achieved by using an ATR FT-IR instrument and observing the sulfur-oxygen and/or carbon-fluorine stretching region of the infrared (IR) spectrum of the aqueous solution. However, when the amount of PFS anions present in water is low, the IR signals are weak, thus making the IR analysis difficult. The present invention overcomes 30 this limitation by providing an ATR sensing element which comprises an extractant compound that has a higher affinity for PFS anions than it has for the nitrate or chloride anion. The extractant compound on the ATR sensing element increases the effective concentration of PFS anions on the ATR sensing element by PFS anion/nitrate anion exchange, thereby leading to a stronger IR signal for the PFS anion. It should be

appreciated that the presence of the extractant compound on the ATR sensing element does not increase the total amount of PFS anions in the aqueous sample but rather provides a higher local concentration of PFS anions on the ATR sensing element relative to the concentration of PFS in the aqueous solution.

5 The extractant compound can be placed onto the ATR sensing element temporarily or permanently. Preferably the extractant compound is placed onto the ATR sensing element permanently by a covalent bond. Moreover, the extractant compound can be placed onto the ATR sensing element by using a linker which is covalently bonded to the extractant compound and the ATR sensing element. Forming a covalent bond
10 between the extractant compound and the ATR sensing element can be achieved by using a variety of methods known in the art. For example, for an ATR sensing element which has silicon oxide on its surface, the surface can be relatively easily modified by using a wide variety of commercially available silanizing agents such as tetraalkyl orthosilicates, such as tetramethyl orthosilicate ($\text{Si}(\text{OCH}_3)_4$) and tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$);
15 tetrachlorosilane (SiCl_4); alkyltrichlorosilanes (RSiCl_3); alkyltrialkoxysilanes ($\text{RSi}(\text{OR}')_3$); dialkyldichlorosilanes (R_2SiCl_2); and dialkyldialkoxysilanes ($\text{R}_2\text{Si}(\text{OR}')_2$). Exemplary methods of placing a polymer onto an ATR sensing element are disclosed in numerous references, including by Han *et al.*, *Applied Spectroscopy*, 1998, 52, 119-122; Regan *et al.*, *Anal. Chim. Acta.*, 1996, 334, 85-92; Lee and Saavedra, *Anal. Chim. Acta.*,
20 1994, 285, 265-269; Taga *et al.*, *Anal. Chem.*, 1994, 66, 35-39; Ruddy and McCabe, *Applied Spectroscopy*, 1990, 44, 1461-1463; Wexler *et al.*, *Chem. Mater.*, 1995, 7, 1583-1588; Ferrer *et al.*, *Mikrochim. Acta. Suppl.*, 1997, 14, 297-299; Kujawski *et al.*, *J. Appl. Polymer Sci.*, 1992, 44, 951-958; and Kubicki *et al.*, *Environ. Sci. Technol.*, 1997, 31, 1151-1156, all of which are incorporated herein by reference in their entirety.

25 Covalent modification can be performed directly on the surface of the ATR crystal. See for example, Mizaikoff *et al.* "FTIR-microspectroscopic investigation of chemisorbed silanes on IR-transparent materials," *Fresenius J. Anal. Chem.* 1993, 346, 355-357, which is incorporated herein by reference in its entirety. By first hydroxylating the surface of a silicon ATR crystal with a strong base (e.g., NaOH or KOH), the
30 hydroxylated surface can then be reacted with an appropriately modified extractant molecule. Such modified extractant molecules typically contain functional groups such as siloxy ($\text{Si}-\text{OR}$), chlorosilyl ($\text{Si}-\text{Cl}$), or other reactive moieties, which are known to readily react with hydroxylated silicon surfaces. An example of such a reaction is illustrated below.



Alternatively, the coating for the ATR crystal (or film) can be a composite material of an R²ER extractant chemically bonded or physically trapped in a layer of nanoporous SiO₂ or another metal oxide prepared using sol-gel techniques. The "R²ER-sol-gel" coating can vary in thickness from a fraction of a micron to several microns, depending on the application.

There are several examples of ATR crystals being modified using the sol-gel method. See for example, Yang et al., "Fabrication and characterization of low-loss, sol-gel planar waveguides," *Anal. Chem.* 1994, 66, 1254-63; Yang et al. "Chemical sensing using sol-gel derived planar waveguides and indicator phases," *Anal. Chem.* 1995, 67, 1307-14; Wexler et al. "Conductive thin-film composite hydrogels: trapping anionic polyelectrolyte polyaziridine host matrix," *Chem. Mater.* 1995, 7, 1583-8; and Lu et al. "Chemical sensors based on hydrophobic porous sol-gel films and ATR-FTIR spectroscopy," *Sens. Actuators, B* 1996, B36, 517-521, all of which are incorporated herein by reference in their entirety. A general method for preparation of sol-gel coated crystals by a variety of silanizing agents, such as RSi(OR')₃, R₂Si(OR')₂, Si(OR')₄, SiCl₄, and similar compounds (R, R' = Me, Et, alkyl), are described below.

A sol-gel is prepared by mixing appropriate ratios of silanizing agent(s), water, acid and extractant (HEP, DEC, other) together. This gel is allowed to condense for an appropriate amount of time before coating onto the surface of the ATR crystal. Coating can be done by a variety of methods including spin coating, dip coating, or drop coating. Upon coating, the crystal is then heated to promote further condensation of the gel, which results in the final, porous coating. The final coating contains the extractant, which is trapped in the pores of the sol-gel.

Furthermore, ATR surfaces may also be modified using a combination of sol-gel and surface modification techniques described above. See for example, Han et al. "Chemical sensors based on surface-modified sol-gel-coated infrared waveguides," *Appl. Spectrosc.*, 1998, 52, 119-122, which is incorporated herein by reference in its entirety. A non-extractant containing sol-gel layer can be coated on a crystal as described above. The sol-gel layer, which has Si-OH moieties on the surface and in the pores, is then

covalently modified with the same modified extractant molecules used for the direct surface modification described above.

Still alternatively, the coating for the ATR crystal can be a composite material of an R^2ER extractant chemically bonded or physically trapped in a layer of an organic or inorganic polymer. The " R^2ER -polymer" coating can vary in thickness from a fraction of a micron to several microns, depending on the application. The polymers used can be simple "carriers" for the R^2ER extractant or they can be designed to enhance the sensitivity of the coating for particular analytes.

Preferably, the extractant compounds are redox-recyclable extractant compounds. As used herein, a "redox-recyclable extractant compound" refers to an extractant compound which can be deactivated and reactivated by reduction and oxidation, respectively. For example, typically the extractant compound is a neutral compound which is oxidized (*i.e.*, activated) to a cation with a corresponding anion. When this oxidized extractant compound is contacted with an aqueous solution containing PFS anions, it undergoes exchange of anions, thereby concentrating PFS anions onto the ATR sensing element. After the analysis, PFS anions can be removed from the ATR sensing element by simply reducing (*i.e.*, deactivating) the extractant compound to regenerate the neutral extractant compound. In this manner, the ATR sensing element can be activated and deactivated rapidly and can be reused repeatedly.

The extractant compounds of the present invention can be reduced or oxidized using a chemical reducing or oxidizing agent, respectively, or by electrochemically. Exemplary chemical oxidizing agents include ferric nitrate, peroxide ion, hypochlorite ion (*i.e.*, household bleach), and cerium(IV) compounds. Preferably, the oxidizing agent is selected from the group consisting of ferric nitrate, hypochlorite ion, and cerium(IV) compounds, more preferably from the group consisting of ferric nitrate and cerium(IV) compounds, and most preferably the chemical oxidizing agent is ferric nitrate. Exemplary chemical reducing agents include ferricyanide ion, dithionite ion, zinc and other active metals, and borohydride ion. Preferably, the reducing agent is selected from the group consisting of ferricyanide ion, dithionite ion, and zinc, more preferably from the group consisting of ferricyanide ion and dithionite ion, and most preferably from the group consisting of dithionite ion. It should be appreciated that when a cation analysis is desired, an appropriate extractant compound is reduced to produce an anion with a corresponding cation.

5 The activated (or ionized) extractant compound can be composed of a cation extractant instead of an anion extractant such as $\text{HEP}^+\text{NO}_3^-$ and $\text{DEC}^+\text{NO}_3^-$. Exemplary cation extractants include $\text{Na}[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-(3)-1,2-C}_2\text{B}_9\text{H}_9(n\text{-C}_{12}\text{H}_{25})_2)]$ ($\text{Na}^+\Gamma$) and $\text{Na}[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-(3)-1,2-C}_2\text{B}_9\text{H}_7(n\text{-C}_{12}\text{H}_{25})_2\text{-9,12-Br}_2)]$, which are described in Clark et al., "Design and Use of a Redox-Recyclable Organometallic Extractant for the Cationic Radionuclides $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$," *Environ. Sci. Technol.* 1999, 33, 2489-2491, which is incorporated herein by reference in its entirety.

10 The extractant compounds of the present invention are selected depending on a particular ion to be analyzed. Generally, extractant compounds are organometallic compounds (e.g., transition-metal complexes) that are stable as neutral complexes and as one-electron oxidized or reduced cations or anions, respectively. Extractant compounds of the present invention are kinetically inert to substitution in both redox states. Preferably extractant compounds include polydentate ligands. Moreover, it is also preferred that the extractant compounds do not contain acid- or base-labile functional groups. In addition, they have redox potentials that allow the use of simple, inexpensive oxidants or reductants and undergo rapid one-electron oxidation or reduction. However, they do not undergo over-oxidation or over-reduction in the presence of an excess of oxidant or reductant. Preferably, the extractant compounds are relatively nontoxic (e.g., iron complexes are preferred to chromium complexes). In addition, they are relatively inexpensive (e.g., iron complexes are preferred to ruthenium complexes). Furthermore, the extractant compounds have negligible water solubility in both working oxidation states.

25 In one particular aspect of the present invention for analyzing weakly-hydrated anions, such as PFS anions, the ionized extractant compound (i.e., activated extractant compound) is selected from salts of large, lipophilic cations having small hydrophilic counter anions. Without being bound by any theory, it is believed that the large lipophilic extractant compound increases the selectivity of the extractant compound for a large counterion that is to be detected. In one particular embodiment of the present invention, the extractant compound is a compound of formula I shown above. Preferably, the extractant compound is 1,1'3,3'-tetrakis(2-methyl-2-hexyl)ferrocenium cation (HEP^+) which contains small hydrophilic counter anions such as nitrate (NO_3^-) or chloride (Cl^-).

30 Preferably, the amount of extractant compound coated onto the surface of the ATR sensing element allows sufficient interaction between the extractant compound

and aqueous PFS anions, thereby increasing the PFS anion concentration in the region sampled by the evanescent wave by the ATR sensing element. The lipophilic portion of the extractant compound serves to reduce or eliminate water from the region sampled by the evanescent wave, which reduces IR radiation absorption by water molecules. For PFS anion analysis using $\text{HEP}^+\text{NO}_3^-$ as the activated extractant compound, a thin film of from about 0.3 μm to about 2 μm thickness of the extractant compound is preferred.

By using a detection probe coated with the extractant compound of the present invention, the sensitivity of the detection probe can be increased by a factor of at least about 100 compared to a detection probe which is not coated with the extractant compound. Preferably, the sensitivity of the coated detection probe is increased by a factor of at least about 1000, more preferably by a factor of at least about 10,000, and most preferably by a factor of at least about 100,000.

Additional objects, advantages, and novel features of this invention will become apparent to those skilled in the art upon examination of the following examples thereof, which are not intended to be limiting.

EXAMPLES

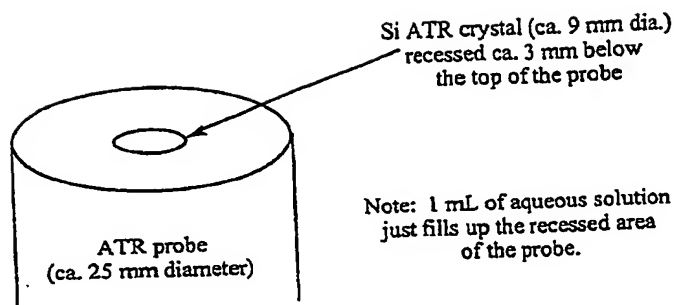
General Procedure

$\text{HEP}^+\text{NO}_3^-$ can be prepared using the procedure disclosed in Clark *et al.*, *Environ. Sci. Technol.*, 1996, 30, 3124-3127 and references cited in Chambliss *et al.*, *Anal. Chem.*, 1998, 70, 757-765, all of which are incorporated by reference herein in their entirety.

An ATR sensing element can be coated with temporary film of $\text{HEP}^+\text{NO}_3^-$ by contacting the ATR sensing element with a dichloromethane solution of $\text{HEP}^+\text{NO}_3^-$ and evaporating the solvent.

IR absorbance was measured using ASI React 1000 FTIR spectrometer (Millersville, MD) with a "30 bounce" SiComp[®] (silicon) probe.

The particular ATR probe that was used for these experiments has approximate dimensions shown in the figure below.



Note: 1 mL of aqueous solution just fills up the recessed area of the probe.

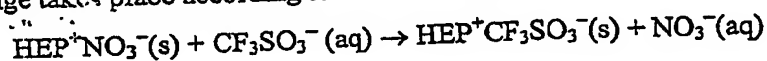
Example 1

This example shows comparison of IR absorbances by 1 mM aqueous solution of $\text{Li}^+\text{CF}_3\text{SO}_3^-$ between an ATR IR sensing element coated with $\text{HEP}^+\text{NO}_3^-$ and an ATR IR sensing element that is not coated with $\text{HEP}^+\text{NO}_3^-$.

About 1 mL of an aqueous solution of 1 mM $\text{Li}^+\text{CF}_3\text{SO}_3^-$ was placed on the unmodified (*i.e.*, not coated with $\text{HEP}^+\text{NO}_3^-$) SiComp[®] (silicon) ATR sensing element and IR absorbance of the solution was measured. A spectrum of water was taken as the background. The resolution was set to 8 cm^{-1} with 128 scans for the Fourier transform function. At these instrumental settings and concentration, there are no noticeable peaks that are characteristic of the triflate molecule. There are four peaks (1266 , 1227 , 1155 , 1034 cm^{-1}) that are unique to triflate from both the C-F and S-O stretching vibrations of the molecule. As shown in Fig. 1, the IR spectrum had a poor signal to noise ratio, and the absorbance at about 1266 cm^{-1} was about 1×10^{-3} .

The procedure was repeated using the ATR sensing element coated with a temporary thin film of $\text{HEP}^+\text{NO}_3^-$. The sensor was coated with a film evaporated from 0.025 mL of a 1 mM $\text{HEP}^+\text{NO}_3^-$ solution in dichloromethane (ACS grade). The resolution was set to 8 cm^{-1} with 128 scans for the Fourier transform function. As shown in Fig. 2, the absorbance of the solution at about 1266 cm^{-1} grew to more than 0.9 within 15 minutes.

Comparison of IR absorption peak at about 1340 cm^{-1} (not shown) indicated a corresponding decrease in the IR peak at 1340 cm^{-1} due to decrease in NO_3^- anion concentration near the ATR sensing element. It is believed that when an aqueous solution of 1 mM $\text{Li}^+\text{CF}_3\text{SO}_3^-$ is placed in contact with the thin film of $\text{HEP}^+\text{NO}_3^-$ an anion exchange takes place according to the following equation:



The exchange of CF_3SO_3^- for NO_3^- is essentially complete because of the selectivity of the HEP^+ cation for large weakly-hydrated anions like CF_3SO_3^- (and other PFS anions) over small strongly-hydrated anions such as NO_3^- .

The detection limit of an FTIR spectrometer for a PFS anion such as CF_3SO_3^- can be increased by a factor of about 10^3 using the present invention. Other weakly-hydrated IR-detectable anions, including but not limited to TcO_4^- , ReO_4^- , and ClO_4^- can also be concentrated and detected.

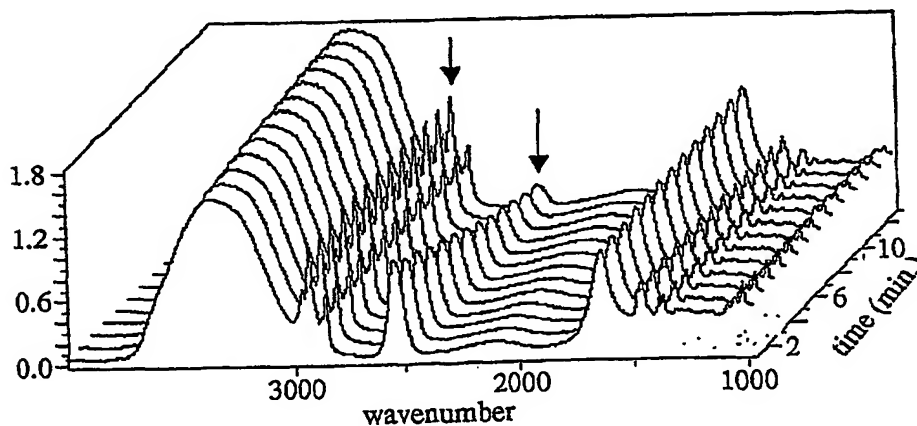
Example 2

This example illustrates the recyclability of the device.

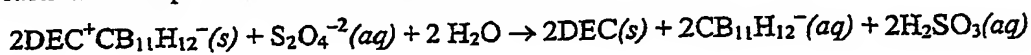
The film of $\text{HEP}^+\text{NO}_3^-$, after undergoing ion-exchange with an aqueous solution of $\text{Li}^+\text{CF}_3\text{SO}_3^-$ was reduced with aqueous $\text{K}_4\text{Fe}(\text{CN})_6$, releasing the CF_3SO_3^- ions and any remaining NO_3^- ions from the film. The film of neutral HEP was then re-oxidized (reactivated) to $\text{HEP}^+\text{NO}_3^-$ with aqueous $\text{Fe}(\text{NO}_3)_3$ in 0.1 M HNO_3 .

Example 3. Redox-recycling of the extractant in the ATR coating.

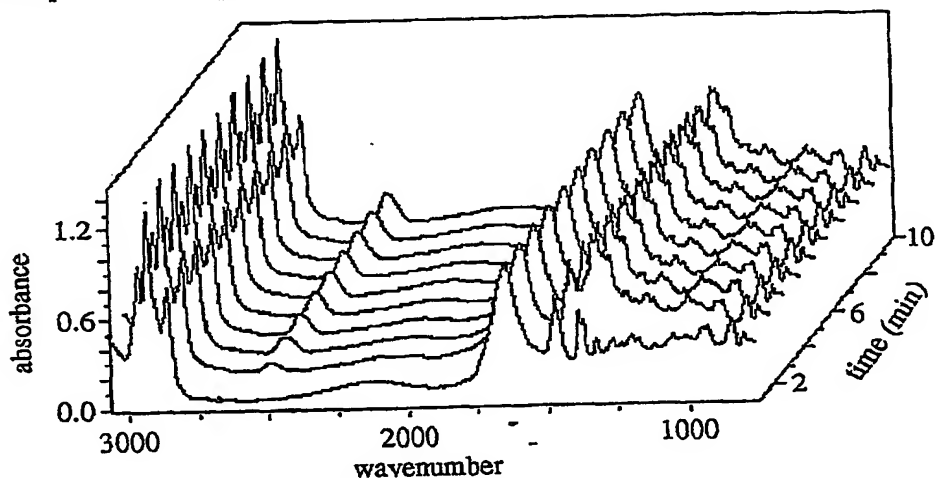
A film of $\text{DEC}^+\text{CB}_{11}\text{H}_{12}^-$ was deposited on the silicon ATR crystal from a dichloromethane solution of the compound. This compound exhibits an intense $\nu(\text{BH})$ band in the IR spectrum at 2540 cm^{-1} . After evaporation of dichloromethane, the film-coated crystal was treated with 1 mL of an aqueous solution containing ca. 0.1 M $\text{Na}_2\text{S}_2\text{O}_4$, a strong reducing agent. IR spectra showed that the intense band at 2540 cm^{-1} decreased over time while the intensities of other bands due to the DEC extractant remained constant over time. This is shown in the figure below.



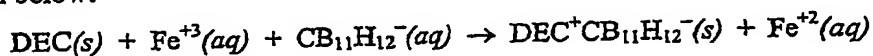
The two bands identified by arrows are at 2930 cm^{-1} (a $\nu(\text{CH})$ band of the $\text{DEC}^{+/0}$ moiety) and at 2540 cm^{-1} . These spectra indicate that $\text{DEC}^+\text{CB}_{11}\text{H}_{12}^-$ in the ATR coating is reduced to DEC with concomitant release of the $\text{CB}_{11}\text{H}_{12}^-$ anion to the aqueous solution. This process, shown in the chemical equation below, represents the deactivation step of an R^2ER -extractant-containing ATR crystal coating:



After the $\nu(\text{BH})$ band of $\text{CB}_{11}\text{H}_{12}^-$ at 2540 cm^{-1} had all but decayed down to the baseline, the film was treated with 1 mL of an aqueous solution containing 0.1 M $\text{Fe}(\text{NO}_3)_3$ (an oxidizing agent) and ca. 10 mM $\text{Cs}^+\text{CB}_{11}\text{H}_{12}^-$. IR spectra showed that the 2540 cm^{-1} band grew back in over time as the film was reactivated (i.e., as the DEC extractant was reoxidized to DEC^+), as shown in the figure below. Note that in the figure, the reactivation step and the concomitant detection of aqueous $\text{CB}_{11}\text{H}_{12}^-$ were combined into one step in this example.

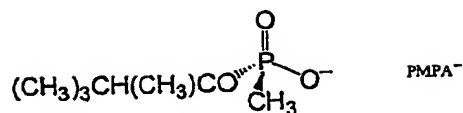


The reactivation/detection process is depicted in the following chemical equation below:



Example 4. Detection of 1 mM aqueous PMPA⁻.

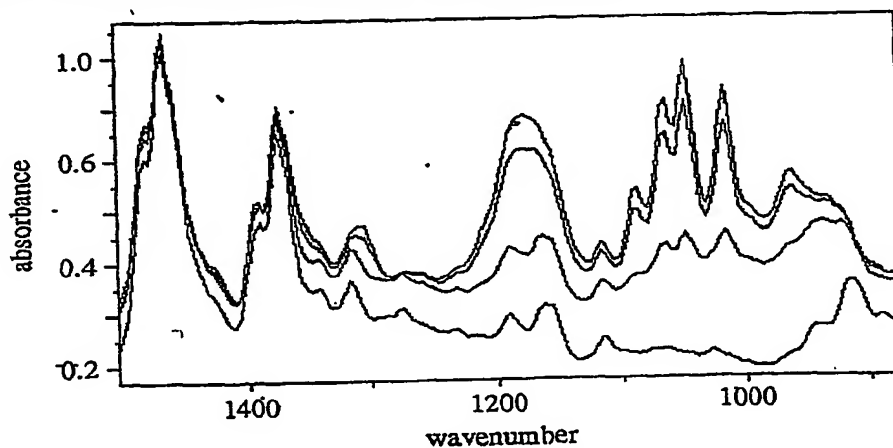
This anion, the structure of which is shown below, is the initial hydrolysis product of the organophosphorus nerve agent GD and is related to the hydrolysis products of other organophosphorus nerve agents such as GA, GB, and VX. Their detection in aqueous media is an important challenge to the U.S. Department of Defense.



A film of $\text{DEC}^+\text{HSO}_4^-$ was deposited on the ATR crystal from a dichloromethane solution of the compound. After evaporation of dichloromethane, the probe was treated with 1 mL of an aqueous solution containing 1 mM PMPA^- . Two of the IR bands of the PMPA^- anion at 1204 and 1065 cm^{-1} were observed by IR spectroscopy within 2 min. Significantly, these two bands were not observed (i.e., 1 mM PMPA^- was not detected) when the uncoated silicon ATR probe was used. The two bands continued to increase in intensity over time. This example demonstrates that the PMPA^- anion can be detected in aqueous media at concentrations below which the anion cannot be detected using an uncoated ATR crystal.

Example 5. Alternative detection of 1 mM aqueous PMPA^- .

A film of DEC^+Cl^- was deposited on the ATR crystal from a dichloromethane solution of the compound. After evaporation of dichloromethane, the probe was treated with 1 mL of an aqueous solution containing 1 mM PMPA^- plus 2 mM acrylamide. IR bands of the acrylamide/ PMPA^- complex at 1177, 1085, 1061, 1040, 1015, 961 cm^{-1} were observed within 2 min. These bands, as well as others, continued to increase in intensity over time, as shown in the figure below.



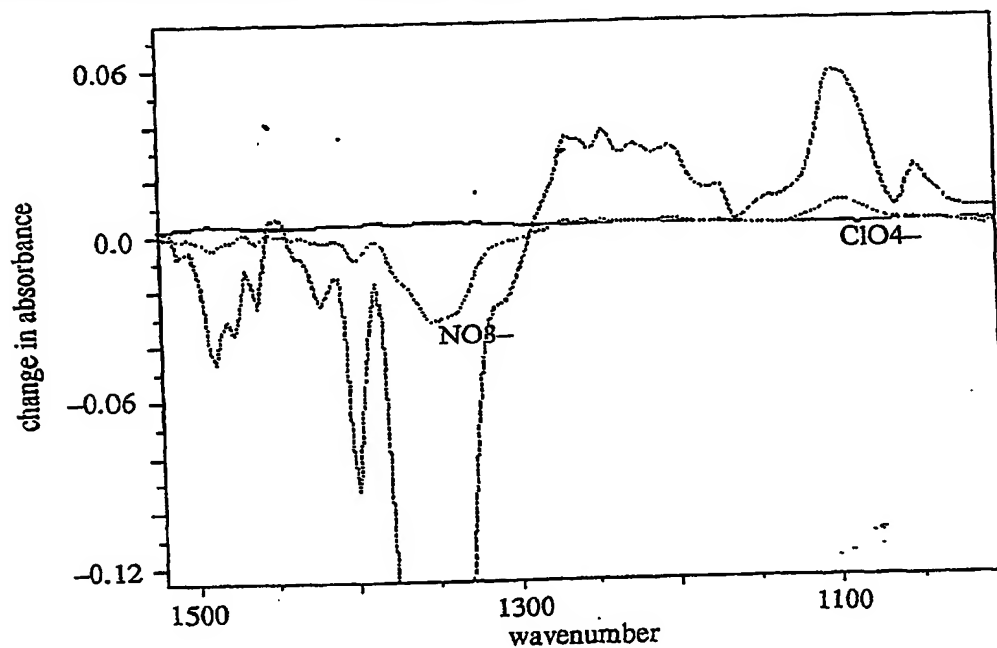
As in Example 4, the PMPA^- bands were not observed when an uncoated silicon ATR probe was treated with the same aqueous solution.

Example 6. Detection of 15 ppb aqueous ClO_4^- .

The perchlorate anion is a groundwater contaminant of growing concern. The U.S. EPA has just finalized the new standard method, based on ion chromatography, for the determination of perchlorate in drinking water. There is no published method based on IR spectroscopy for determining ppm and lower concentrations of ClO_4^- in water. There are many advantages of $\text{R}^2\text{ER-ATR-FTIR}$ detection over ion chromatographic detection of ClO_4^- in water including:

- (1) the $\nu(\text{ClO})$ band at 1094 cm^{-1} is directly observed, so false readings due to a similar retention time for a co-contaminant are avoided;
- (2) sample pre-treatment is avoided (this is frequently necessary for ion chromatography when the ionic strength of the sample is high); and
- (3) the probe can be quickly (within minutes) deactivated and reactivated for the next sample.

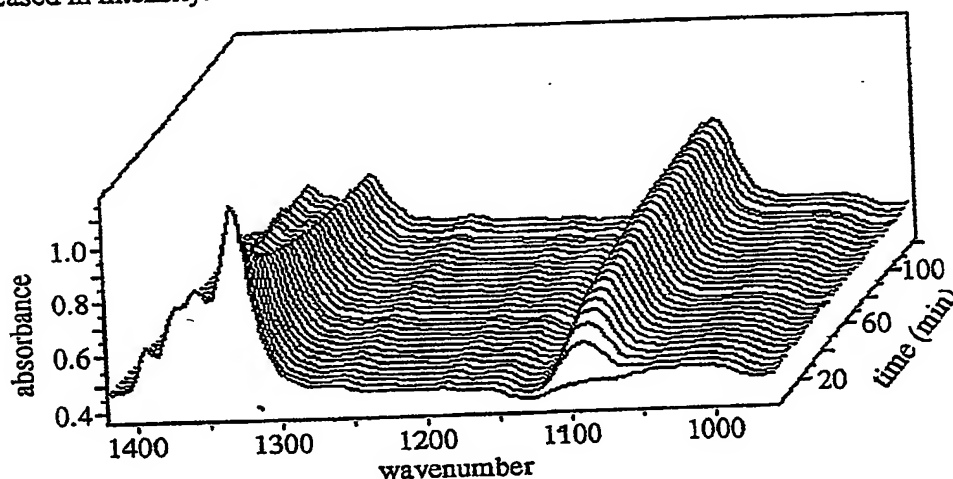
A film of $\text{DEC}^+\text{NO}_3^-$ was deposited on the ATR crystal from a dichloromethane solution of the compound. After evaporation of dichloromethane, the probe was treated with 1 mL of an aqueous solution containing 15 ppb ClO_4^- (potassium salt). The intensity of the IR band due to the NO_3^- ion in the film decreased over time while the $\nu(\text{ClO})$ IR band at 1092 cm^{-1} grew in over time, as shown in the difference ATR-FTIR spectra displayed in the figure below.



The $\nu(\text{ClO})$ band due to ClO_4^- grows in at 1092 cm^{-1} because ClO_4^- is accumulating in the film (i.e., it is undergoing selective ion exchange with NO_3^- originally in the film). The negative band at 1360 cm^{-1} is the $\nu(\text{NO})$ band of NO_3^- , which is partitioning from the film into the aqueous sample. Since the detection limit of ClO_4^- with the uncoated silicon ATR crystal is 230,000 ppb, this example demonstrates that a lowering of the detection limit by a factor of more than 10,000 is possible using R^2ER -extractant-containing coatings on FTIR ATR crystals.

Example 7. Detection of 1 ppm aqueous ClO_4^- .

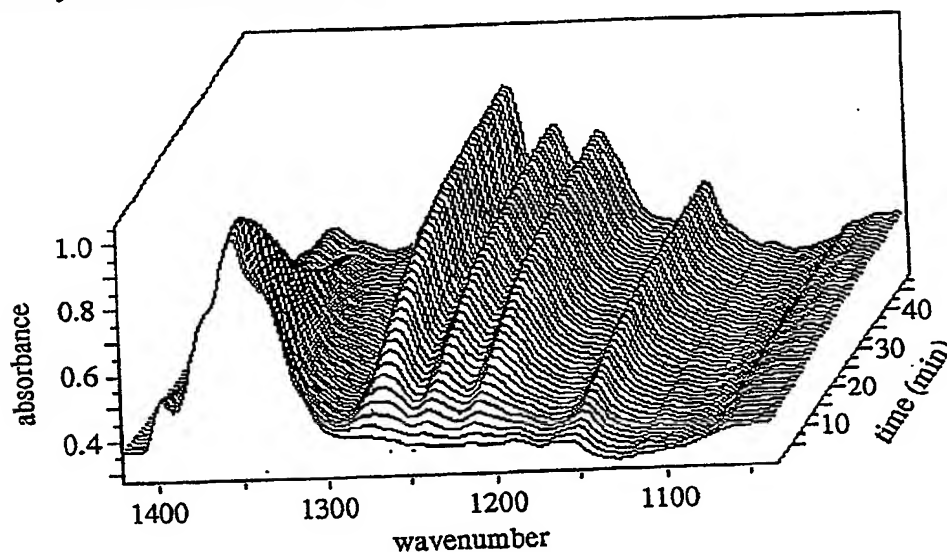
The method used was the same as in Example 6 except that the aqueous solution contained only 1 ppm ClO_4^- (potassium salt). As can be seen in the figure below, the ClO_4^- peak at 1092 cm^{-1} grew in over time as the NO_3^- peak at 1351 cm^{-1} decreased in intensity.



Example 8. Detection of 5 μM aqueous $\text{C}_8\text{F}_{17}\text{SO}_3^-$.

A film of $\text{DEC}^+\text{NO}_3^-$ was deposited on the ATR crystal from a dichloromethane solution of the compound. After evaporation of dichloromethane, the probe was treated with 1 mL of an aqueous solution containing 5 μM $\text{C}_8\text{F}_{17}\text{SO}_3^-$ (potassium salt). This concentration of the perfluorooctane sulfonate anion is equivalent to 2.5 ppm. As IR spectra were recorded over time, the intense band due to NO_3^- at 1351 cm^{-1} decreased in intensity while four bands due to the $\text{C}_8\text{F}_{17}\text{SO}_3^-$ anion in the $1266\text{--}1150\text{ cm}^{-1}$ region increased over time, as shown in the figure below. The four bands due to the

$C_8F_{17}SO_3^-$ anion were clearly visible after only 10 minutes. This example demonstrates that ppm concentrations of surfactant anions such as $C_8F_{17}SO_3^-$ can be detected within minutes by methods of the present invention.

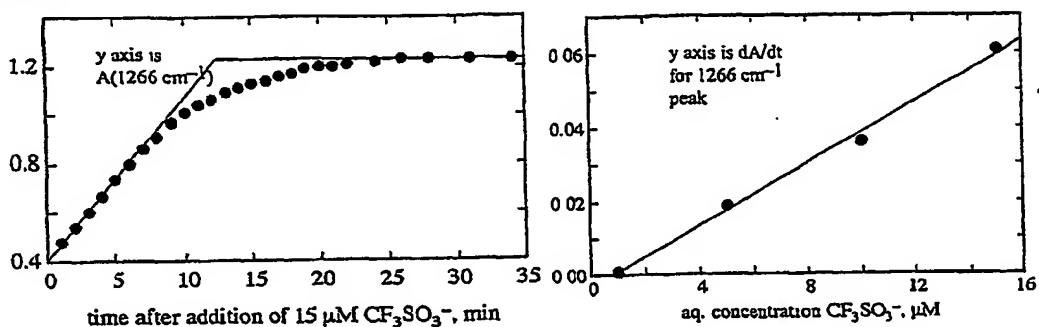


Example 9. Quantitation of μM concentrations of $CF_3SO_3^-$.

A film of $DEC^+NO_3^-$ was deposited on the ATR crystal from a dichloromethane solution of the compound. After evaporation of dichloromethane, the probe was treated with 1 mL of an aqueous solution containing either 1, 5, 10, or 15 μM $CF_3SO_3^-$ (lithium salt). The intensity of one of the IR bands of the $CF_3SO_3^-$ ion, at 1266 cm^{-1} , was monitored over time. Significantly, the final intensity of the $CF_3SO_3^-$ bands are not proportional to the concentration of the analyte, because the R^2ER film has such a high selectivity for weakly hydrated anions that $NO_3^-/CF_3SO_3^-$ ion exchange is complete at nearly all concentrations of $CF_3SO_3^-$. In order to obtain concentration information using coated probe of the present invention, a plot of the rate of change of the absorbance with time was obtained for the initial linear portion of an A vs. t plot (see figure on the left below) versus concentration, as shown in the figure on the right below.

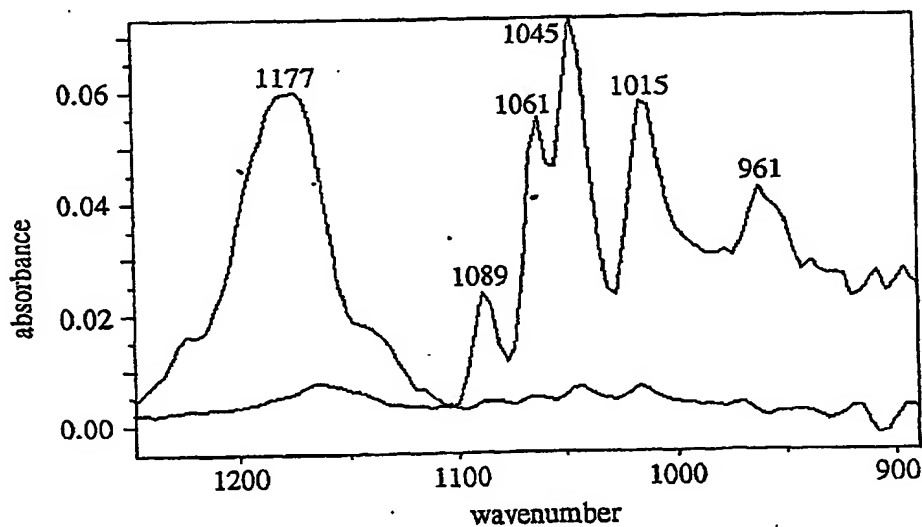
The linear nature of this plot shows that it can be used as a calibration curve to determine an unknown concentration of $CF_3SO_3^-$ in the 1–15 mM concentration range (note that 1 μM $CF_3SO_3^-$ corresponds to 149 ppm $CF_3SO_3^-$). Importantly, when the 15 μM $CF_3SO_3^-$ experiment was repeated with a 10-fold excess of $NaNO_3$ added to the aqueous sample, the dA/dt value was unchanged. This shows that the calibration curve

can be used even when other, more strongly hydrated ions, are present in the aqueous sample.



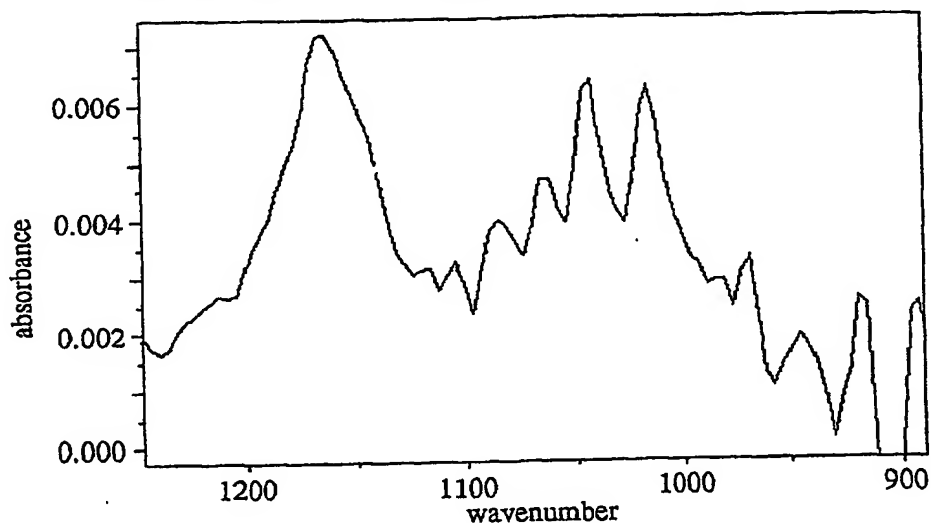
5 Example 10. Detection of 0.1 mM aqueous PMPA⁻.

A film of DEC^+Cl^- was deposited on the ATR crystal from a dichloromethane solution of the compound. After evaporation of dichloromethane, the probe was treated with 100 mL of an aqueous solution containing 0.1 mM PMPA⁻ (this corresponds to 18 ppm PMPA⁻). Six of the IR bands of the PMPA⁻ anion, at 1177, 1089, 1061, 1045, 1015, and 961 cm^{-1} , were observed within minutes. After 30 minutes, a difference spectrum was recorded (the spectrum that was subtracted was that of the DEC^+Cl^- coating at the start of the experiment). This spectrum is shown below.



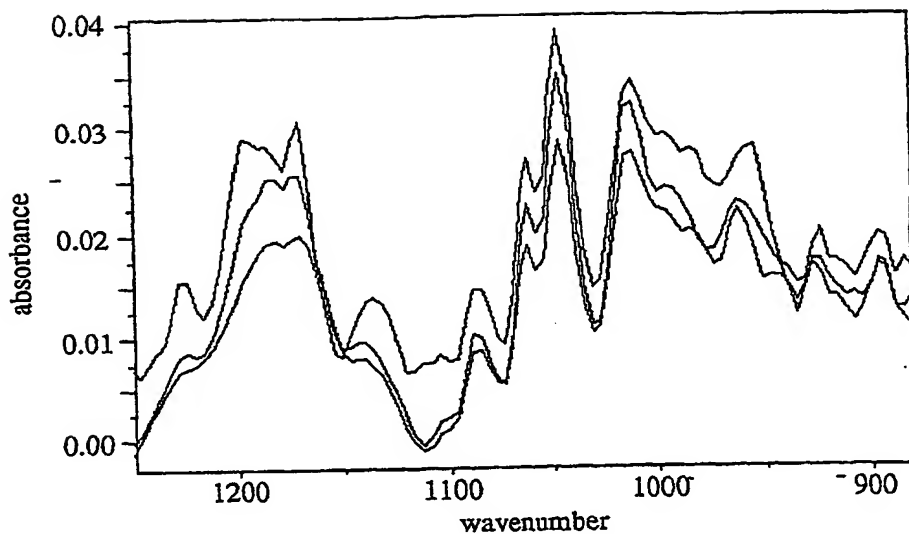
The six PMPA⁻ bands are clearly seen. The maximum absorbance of the most intense bands, at 1177 and 1045 cm^{-1} , are 0.060 and 0.074, respectively. The lower spectrum in the figure below is the spectrum of a 10 mM aqueous solution of PMPA⁻ (i.e., the free acid at pH 7.3) with an *uncoated* silicon ATR probe. Note that the bands of

the PMPA⁻ anion are barely visible in the lower spectrum even though the concentration of the anion is 100 times greater than in the experiment with the coated ATR probe. The spectrum of 10 mM aq. PMPA⁻ with an expanded vertical scale is shown below.



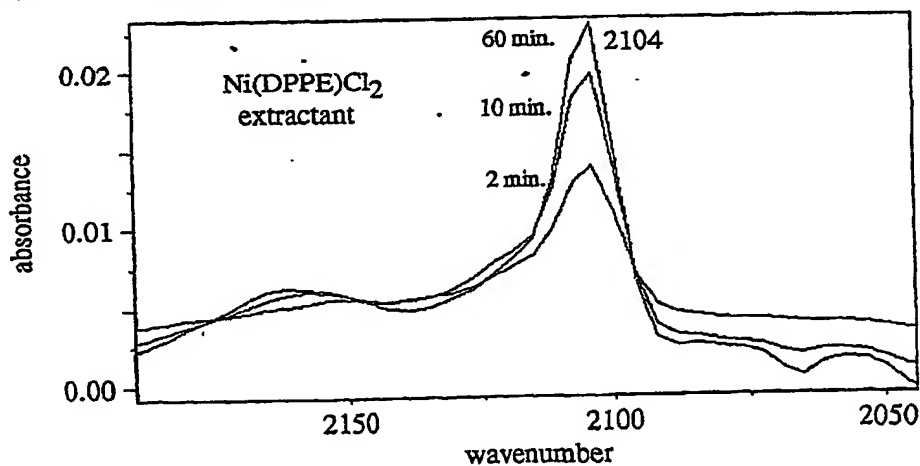
Example 11. Detection of 0.01 mM aqueous PMPA⁻

A film of DEC⁺Cl⁻ was deposited on the ATR crystal from a dichloromethane solution of the compound. After evaporation of dichloromethane, the probe was treated with 100 mL of an aqueous solution containing 0.01 mM PMPA⁻ (this corresponds to 2 ppm PMPA⁻). Six of the IR bands of the PMPA⁻ anion, at 1177, 1089, 1061, 1045, 1015, and 961 cm⁻¹, were observed within minutes. After 10, 30 and 60 minutes, difference spectra were recorded (the spectrum that was subtracted was that of the DEC⁺Cl⁻ coating at the start of the experiment). These three difference spectra are shown below. The lowest trace is the 10 minute difference spectrum; the highest trace is the 60 minute difference spectrum. Note that 2 ppm aq. PMPA⁻ can be detected in 10 minutes.



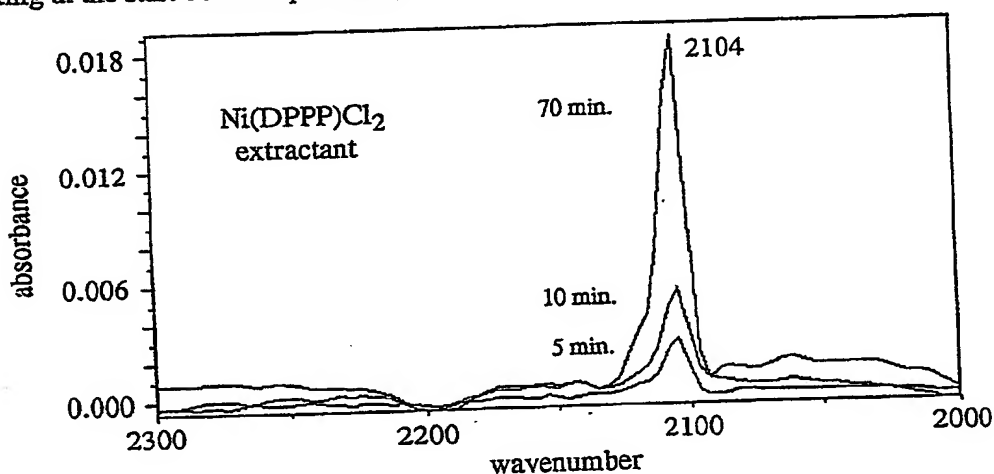
Example 12. Detection of 26 ppm aqueous CN^- .

A film of $\text{Ni}(\text{DPPP})\text{Cl}_2$ was deposited on the ATR crystal from a dichloromethane solution of the compound (DPPP=1,3-bis(diphenylphosphino)propane). After evaporation of solvent, the probe was treated with 1 mL of aqueous 1.00 mM KCN (this corresponds to 26 ppm CN^-). The difference IR spectra shown below indicate that the treated probe can detect 26 ppm CN^- within 2–10 minutes (the spectrum that was subtracted was that of the $\text{Ni}(\text{DPPP})\text{Cl}_2$ coating at the start of the experiment). Note that the $\text{Ni}(\text{DPPP})\text{Cl}_2$ extractant has not yet been demonstrated to be redox-recyclable.



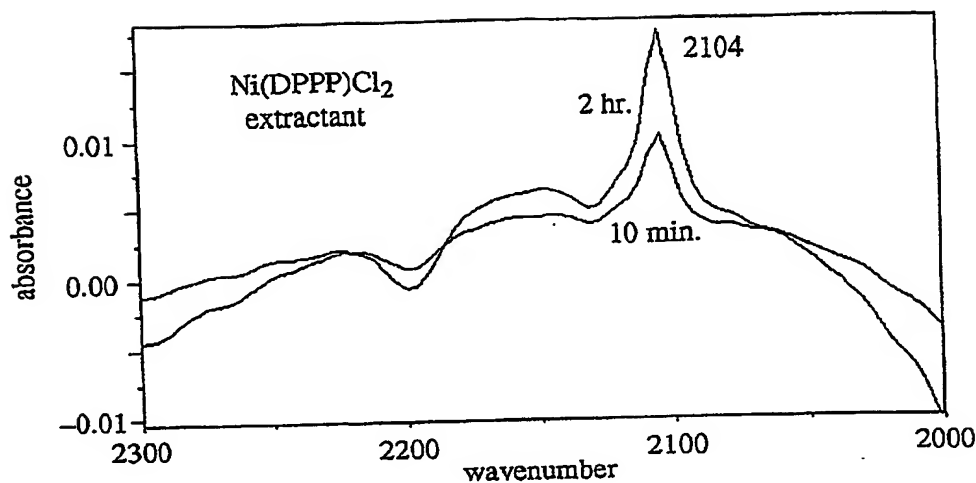
Example 13. Detection of 0.26 ppm aqueous CN^- .

A film of $\text{Ni}(\text{DPPP})\text{Cl}_2$ was deposited on the ATR crystal from a dichloromethane solution of the compound. After evaporation of solvent, the probe was treated with 100 mL of aqueous 0.01 mM KCN (this corresponds to 0.26 ppm CN^-). The difference IR spectra shown below indicate that the treated probe can detect 0.26 ppm CN^- within 5–10 minutes (the spectrum that was subtracted was that of the $\text{Ni}(\text{DPPP})\text{Cl}_2$ coating at the start of the experiment).



Example 14. Detection of 0.26 ppm aqueous CN^- in the presence of 1.0 M Cl^- .

A film of $\text{Ni}(\text{DPPP})\text{Cl}_2$ was deposited on the ATR crystal from a dichloromethane solution of the compound. After evaporation of solvent, the probe was treated with 100 mL of an aqueous solution that contained 0.01 mM KCN (this corresponds to 0.26 ppm CN^-) and 1.0 M NaCl. The difference IR spectra shown below indicate that the treated probe can detect 0.26 ppm CN^- within 10 minutes even though the chloride ion co-contaminant is present in 100,000-fold excess (the spectrum that was subtracted was that of the $\text{Ni}(\text{DPPP})\text{Cl}_2$ coating at the start of the experiment). It is believed that other co-contaminants such as sulfate, bromide, carbonate, and bicarbonate also do not interfere, and therefore it is possible that a probe coated with $\text{Ni}(\text{DPPP})\text{Cl}_2$ or a similar extractant can also detect cyanide in brackish water and seawater.



5 The foregoing discussion of the invention has been presented for purposes of illustration and description. The foregoing is not intended to limit the invention to the form or forms disclosed herein. Although the description of the invention has included description of one or more embodiments and certain variations and modifications, other variations and modifications are within the scope of the invention, *e.g.*, as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative embodiments to the extent permitted, including alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures, functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter.

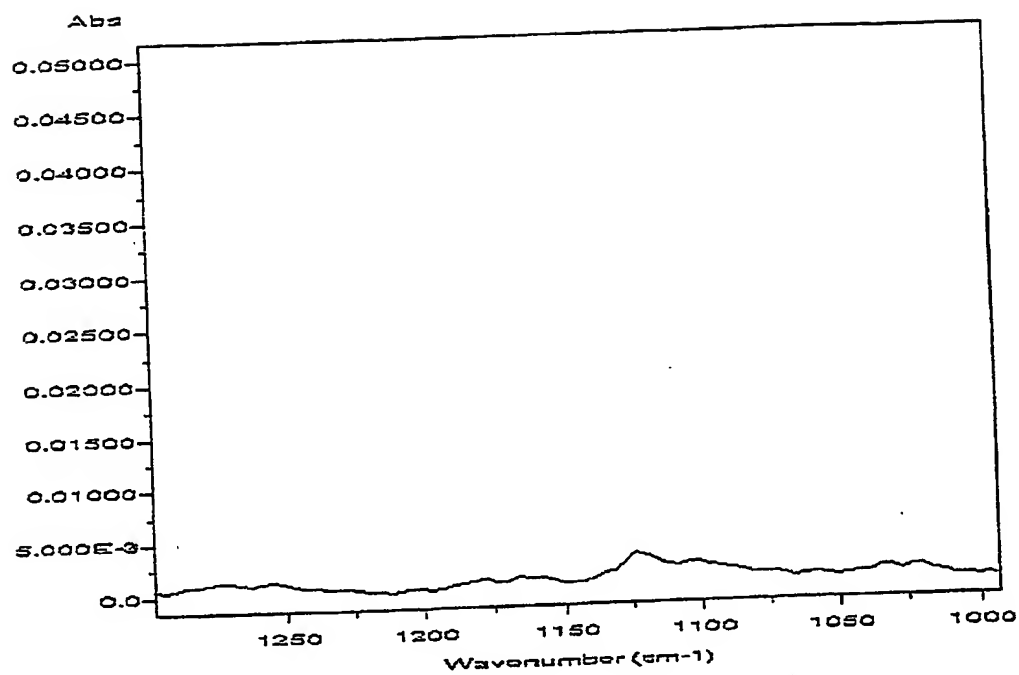


Figure 1

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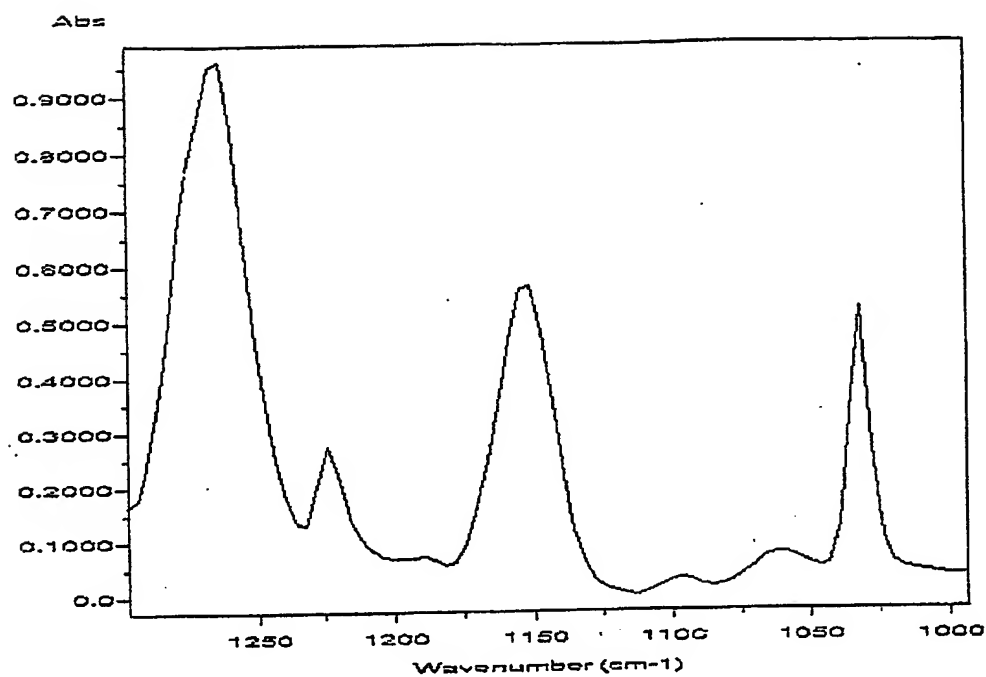


Figure 2

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